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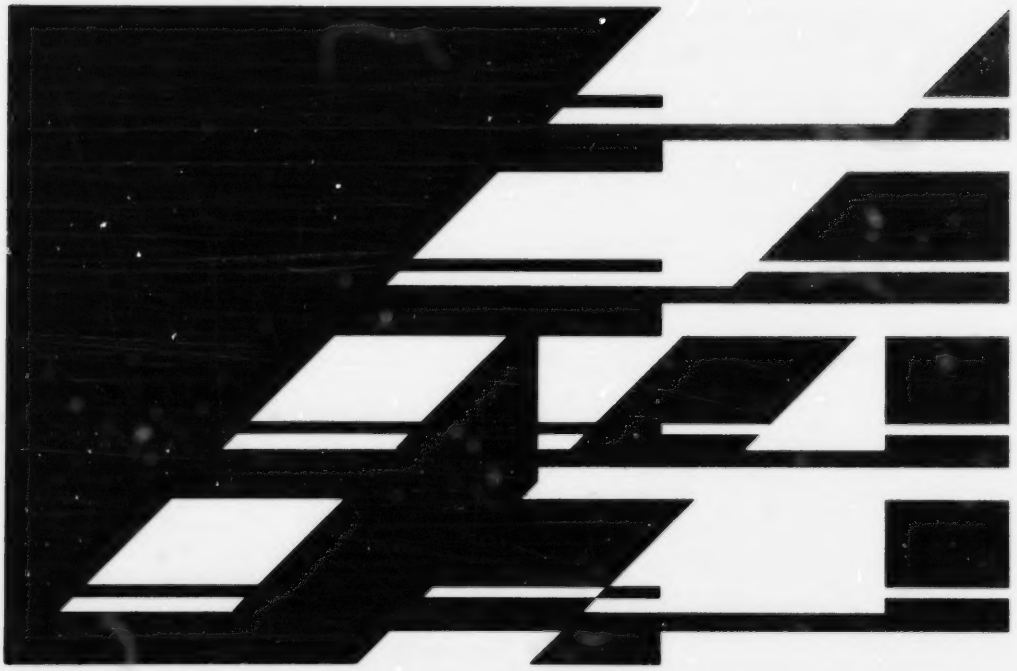

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CONTRACT REPORT NO. OSV83-00065

The Thermodynamics of Arsenic Oxide

by

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September 1987.

ABSTRACT

The vapour species over $As_2O_{3(s)}$ was determined by a Knudsen-mass spectrometric technique. The following ions were detected $As_4O_6^+$, $As_4O_5^+$, $As_3O_4^+$, $As_2O_3^+$ and AsO^+. The corresponding neutral molecules are As_4O_6, As_2O_3 and AsO. The major species is As_4O_6.

The vapour pressure of As_4O_6 was determined over a narrow temperature range 220-270°C. The results agreed well with the literature values.

A review of the thermodynamic data of various arsenic compounds was carried out. A list of recommended data is given.

58pp

MICROMEDIA

INTRODUCTION

Arsenic is a toxic and undesirable element which occurs in non-ferrous metal processing. Its presence in high concentrations can prevent the treatment of certain ores which could otherwise be suitable for feed to Canadian smelters. One of the requirements of the development of effective methods for treating high arsenic ores is reliable thermodynamic data. The development of thermodynamic data would lead to a better understanding of and also assist in the prediction of the behaviour of arsenic in metallurgical processing.

A review of the available literature was carried out to evaluate the thermodynamics of arsenic oxides and sulphides. A listing of the available literature is given in Appendix I.

Arsenic Oxides

The sesqui oxides of arsenic belong to a group of compounds which form several polymorphic modifications (1,2). The stable form at high temperature is the more symmetrical arsenolite (cubic As_2O_3). The monoclinic form is referred to as claudetite. Arsenolite is the crystal which forms on condensation of the vapor phase.

The vapor species over As_2O_3 (s) is the polymer As_4O_6 as determined from vapor density measurements by Biltz (3) and from electron diffraction investigations of the vapor by Maxwell et al. (4). Above 800°C, indications are that the vapor As_4O_6 dissociates to As_2O_3 (g). However, data for this dissociation are not available.

Recently, Brittain, Lau and Hildenbrand (5) indicated from mass spectrometric analysis that there exists a large number of As-O molecular species. They identified As_4O_6, As_4O_5, As_4O_4, As_4O_3, As_2O_3, AsO_2, AsO and As_3O_4 as possible neutral gaseous molecules. However, the formation of many of these species may be due to fragmentation and simple ionization of existing species. Their results are not conclusive.

In this communication, we report our experience with the mass spectroscopic determination of the vapour species above As_2O_3 and the vapour pressure of As_4O_6 as determined by the transportation technique. Finally, the available data on arsenic oxide systems are summarized.

Part I

The mass spectrometric determination of vapor species over $As_2O_3(s)$

Experimental

A Kundsen cell arrangement coupled to a quadrupole mass spectrometer was used to determine the gaseous species over arsenic oxide. As shown in Fig. 1, the cell assembly was constructed from quartz tubing. The overall assembly was kept in a two temperature zone furnace under high vacuum. The Knudsen cell was maintained at temperatures above 800°C while the arsenic oxide sample was maintained at approximately 30-150°C. The sample temperature controlled the arsenic oxide vapor pressure while the Knudsen cell temperature controlled the decomposition pressure. With this design, the As_4O_6 (g) which vaporized from the sample container was directed to the decomposition chamber, the Knudsen cell, held at a higher temperature. The gaseous species which may form are then ionized and analyzed by the mass spectrometer.

Since the apparatus was constructed from quartz, the upper temperature limit was kept at 1100°C. The orifice diameter in the Knudsen cell was approximately 0.76 mm.

The experimental procedure consisted of filling the sample reservoir with approximately 1 gm of As_2O_3. The sample tube was then fused, in the central section, with the Knudsen cell assembly to produce a single reaction tube. This tube was then placed in the two temperature zone furnace tube. The sytem was then evacuated. After reaching a vacuum of approximately 10^{-6} mm Hg, the furnace temperature at the Knudsen cell and sample zone were increased to the desired values.

The alignment of the orifice of the Knudsen cell to the ion source of the mass spectrometer was determined by locating the position of maximum peak height by rotating the alumina sample support.

A series of preliminary tests were carried out to determine the appearance and dissociation potential of all the gaseous species involved in the As-O system between 800 and 1150°C. On this basis, the mass spectrometric measurements were performed using an ionization potential of 12 eV, thus minimizing the effect of polymer dissociation while maintaining it well above the appearance potentials of all gaseous species.

Results and Discussion

A great deal of experimental difficulties were experienced with this project. The high sublimation pressure of the arsenic oxide tended to create an uneven mass flow of volatile oxide from the sample chamber to the high temperature zone. In many experiments, the As_2O_3 in the sample

Table I - Relative intensities of ions detected over As_2O_3 (s)

Temp °C	800	900	1000	1100
Ions				
$As_4O_6^+$	100	100	100	100
$As_4O_5^+$	1-0.2	2-0.2	2-0.2	2-0.2
$As_3O_4^+$	25-10	25-10	15-5	15-2
$As_3O_4^+$	25-10	25-10	15-5	15-2
$As_2O_3^+$	0.7-0.2	2-0.2	5-0.2	5-0.2
AsO^+	0.7-0.2	2-0.2	10-0.2	10-0.2

Table II Corresponding neutral molecule

Ion	Molecule
$As_4O_6^+$	As_4O_6
$As_4O_5^+$	As_4O_6
$As_3O_4^+$	As_4O_6
$As_2O_3^+$	As_4O_6 and As_2O_3
AsO^+	AsO

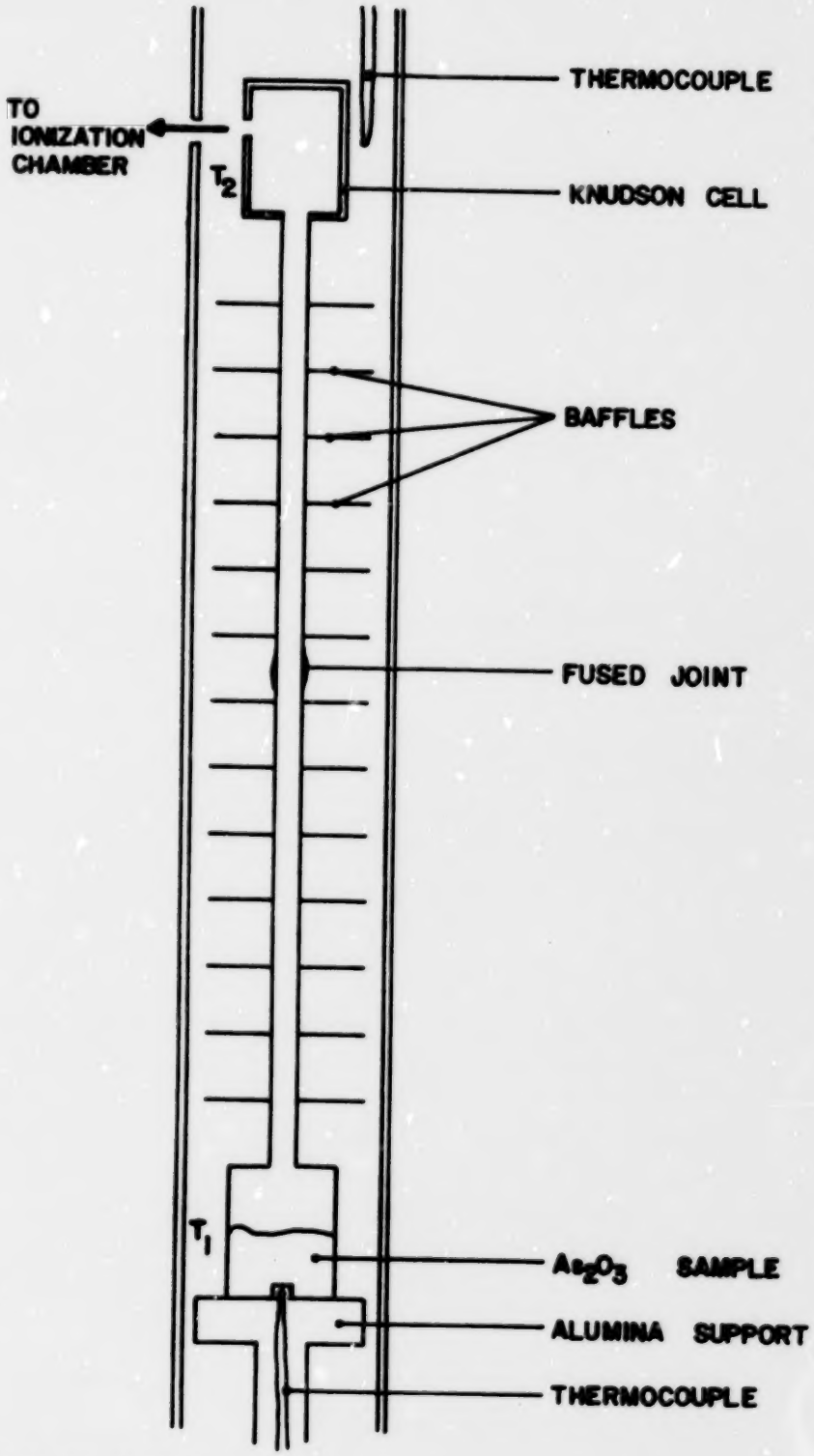

FIGURE 1 DIAGRAM OF APPARATUS

chamber vaporized prior to being detected by the mass spectrometer. With large amounts of As_2O_3 being transferred to the detector unit of the mass spectrometer, contamination of the mass spectrometer became a serious and expensive problem. In spite of these difficulties, it was possible to obtain qualitative results on the species present over As_2O_3 (s).

Table I lists the ions detected and their relative intensities as a function of temperature. The corresponding neutral vapor molecules are listed in Table II.

The ions observed were $As_4O_6^+$, $As_4O_5^+$, $As_3O_4^+$, $As_2O_3^+$ and AsO^+. From the variation in the magnitude of the ionization potential used, $As_4O_6^+$ was determined to be the parent ion. All other ions are the result of fragmentation. The neutral vapor specie As_4O_6 is the major gas molecule and As_2O_3 and AsO are the minor species. With increase in temperature from 800 to 1100°C the As_2O_3 gas species increases, but is still a relatively minor component of the gas phase.

Conclusions

From a qualitative analysis of the mass spectroscopic intensities, As_4O_6 is the major gas species over the temperature range investigated (800-1100°C). However, additional thermodynamically stable neutral gas species As_2O_3 and AsO appear in the vapor phase as temperature is increased.

While the vapor phase is very complex, the form of the condensed phase is always As_2O_3 (s).

Part II

Transportation technique

Since the Knudsen cell-mass spectrometric technique could not give absolute vapor pressures of the various species nor consistent intensities of the various complex gas ions, it was decided to develop a transportation technique to determine the thermodynamics of the As-O system.

Vapor pressure over As_2O_3 (s)

The vapor pressure of arsenolite has been studied by many investigators. Behrens and Rosenblatt (6) have summarized the available data and together with their effusion cell technique proposed the equation

$$\log_{10} P_{atm} = -\frac{(6067 \pm 125)}{T} + (9.905 \pm 0.319)$$

for the temperature range 367-429 K.

In the present study, the pressure over As_2O_3 at selected temperatures were determined (220-270°C). Having determined these values, effort was made to pass these known pressures over samples containing various metal oxide. However, due to mass spectrometric problems this latter work was not possible.

The Transportation Method

This method is the most widely used indirect approach for the measurement of vapor pressure. In this technique, an inert gas (in this study, argon) is passed over a pyrex boat containing arsenic oxide. The argon carrier gas becomes saturated with arsenic oxide vapor which enters into a pyrex condenser tube where the vapor condenses. The flow rate and flow time of the carrier gas are monitored to obtain the total volume passed. From the weight of the oxide collected in the condenser, the vapor pressure of the oxide is obtained from

$$P_{As_4O_6} = P_T \frac{W_{As_2O_3}/2MW_{As_2O_3}}{W_{As_2O_3}/2MW_{As_2O_3} + nt}$$

where $P_{As_4O_6}$ is the partial pressure of As_4O_6 gas, P_T is the atmospheric pressure, $W_{As_2O_3}$ is the weight gain in the condenser tube, $MWAs_2O_3$ is the molecular weight of As_2O_3, n is the flow rate of the carrier gas in mol and t is the flow time.

In order to obtain accurate information for the vapour pressure, it is essential to verify the complete saturation of the carrier gas by the vaporized species. This is obtained by measuring the apparent vapor pressure as a function of flow rate.

Apparatus

The transportation apparatus is shown in Fig. 2. It consists of a quartz outer tube, 1220 mm x 25 mm i.d. A pyrex cell with a cylindrical sample chamber 60mm x 15 mm sits in the quartz tube which was then placed in a cylindrical electrical resistance furnace 35 mm in diameter and 500 mm in length. A pyrex condenser, 7 mm O.D., 5 mm I.D. was placed in the sample chamber to lay flush against the orifice of the chamber. A chromel-alumel thermocouple was placed in the quartz tube near the sample.

A temperature profile for the transportation assembly is shown in Fig. 3.

The gas system accommodated a dry oxygen-free ultra high purity argon. The gas was dried with $CaSO_4$ and oxygen removed by a copper getter furnace at 450°C. A vacuum connection was employed to remove air

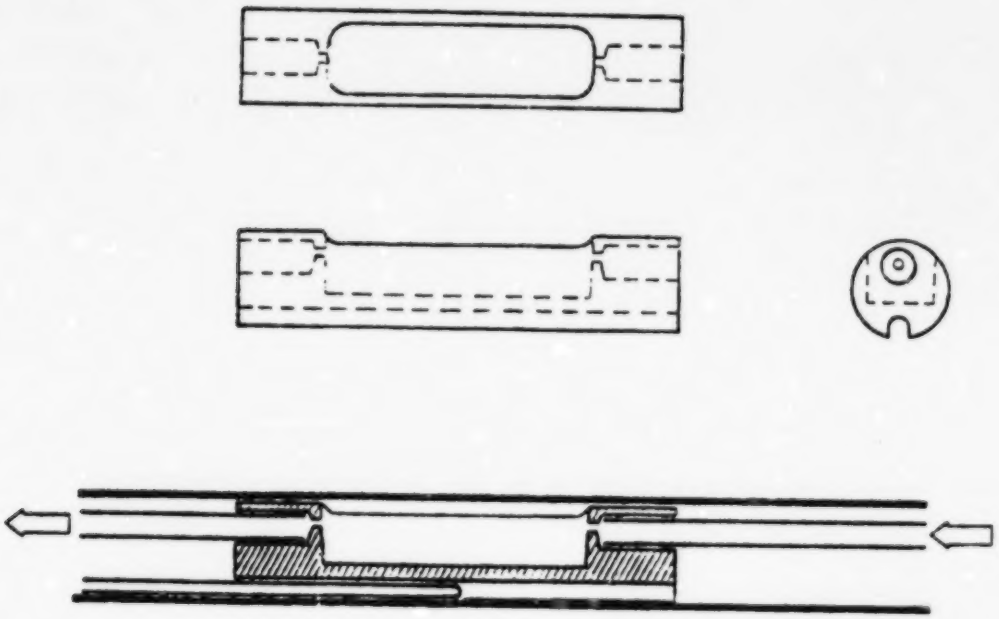

FIGURE 2. A SCHEMATIC DIAGRAM OF THE TRANSPORTATION CELL

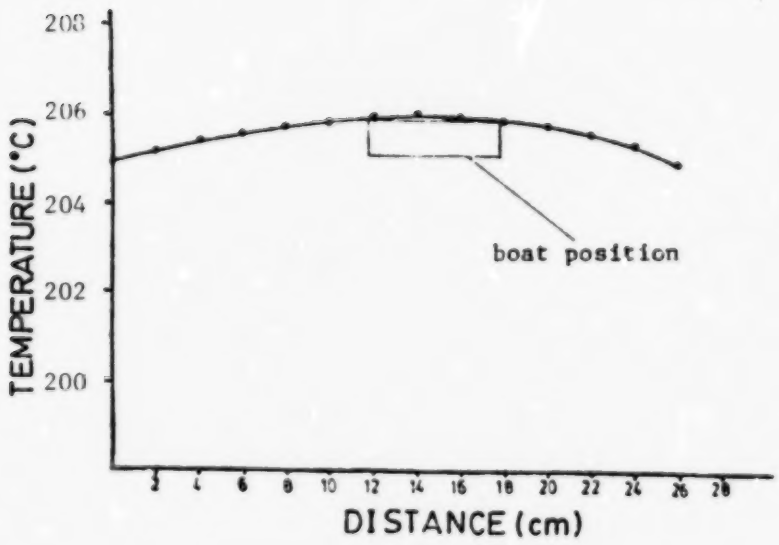

FIGURE 3. THE TEMPERATURE PROFILE OF THE FURNACE

that penetrated the system during the sample loading period.

The total volume of carrier gas was measured as a function of flowrate and time. A plot of HP/T versus n was generated as shown in Fig 4 where

H = height of dibutyl phthalate (m)
P = atmospheric pressure (Pa)
T = room temperature (K)
n = flowrate of argon (mol/s)

Procedure

Reagent grade As_2O_3 (Baker Chemical) was placed in the pyrex sample container. While argon is flowing through the system in a back flush cycle, the As_2O_3 chamber is placed in the quartz outer tube. The condenser tube is then placed flush around the sample chamber orifice. The argon flow is then diverted from the quartz outer tube. The system is evacuated for five minutes to remove any air. The vessel is then pressureized with argon, still on the backflush cycle. This procedure is repeated three times. When the vessel is sufficiently purged, the assembly is loaded into the furnace. As the sample is brought up to temperature, some As_2O_3 is lost due to vaporization. However, the vapor is carried away from the sample chamber to an exhaust condenser. When the experimental temperature is reached, the flow of argon is switched to the forward cycle and the timing begins. The forward cycle is depicted in Fig. 5. The saturated carrier gas transports the vapor to the clean condenser tube. At the completion of the run, the experimental time is recorded and the argon flow is returned to the backflush cycle. The assembly is then removed from the furnace and the cooled condenser tube is weighed.

Saturation of the Carrier Gas

A series of experiments were performed to determine the saturation curve for As_4O_6 at 220°C. The carrier gas flow rates were varied from 1×10^{-5} to 9×10^{-5} mol/s of dry argon. The duration of some of these tests were adjusted to obtain a large weight of condensate, typically from 50 to 150 mg, so that the relative error from weighing would be minimized.

Results and Discussion

A saturation curve for a temperature of 220°C is shown in Fig 6 where the calculated vapor pressure is plotted gainst the flowrate. A plateau region was achieved for argon flowrates in the range of 3.5×10^{-5} to 6.0×10^{-5} mol/s. The vapor pressure of As_4O_6 at saturation was 373.6 Pa.

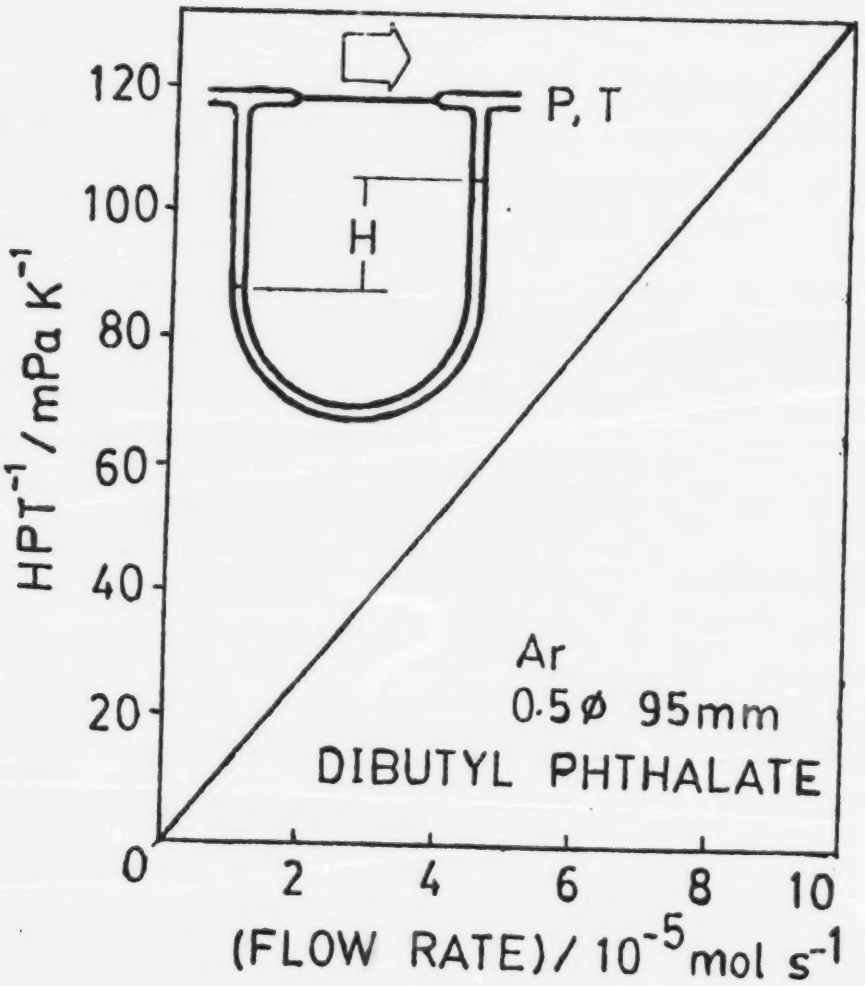

FIGURE 4. THE CALIBRATION CURVE FOR THE FLOWRATE OF ARGON GAS.

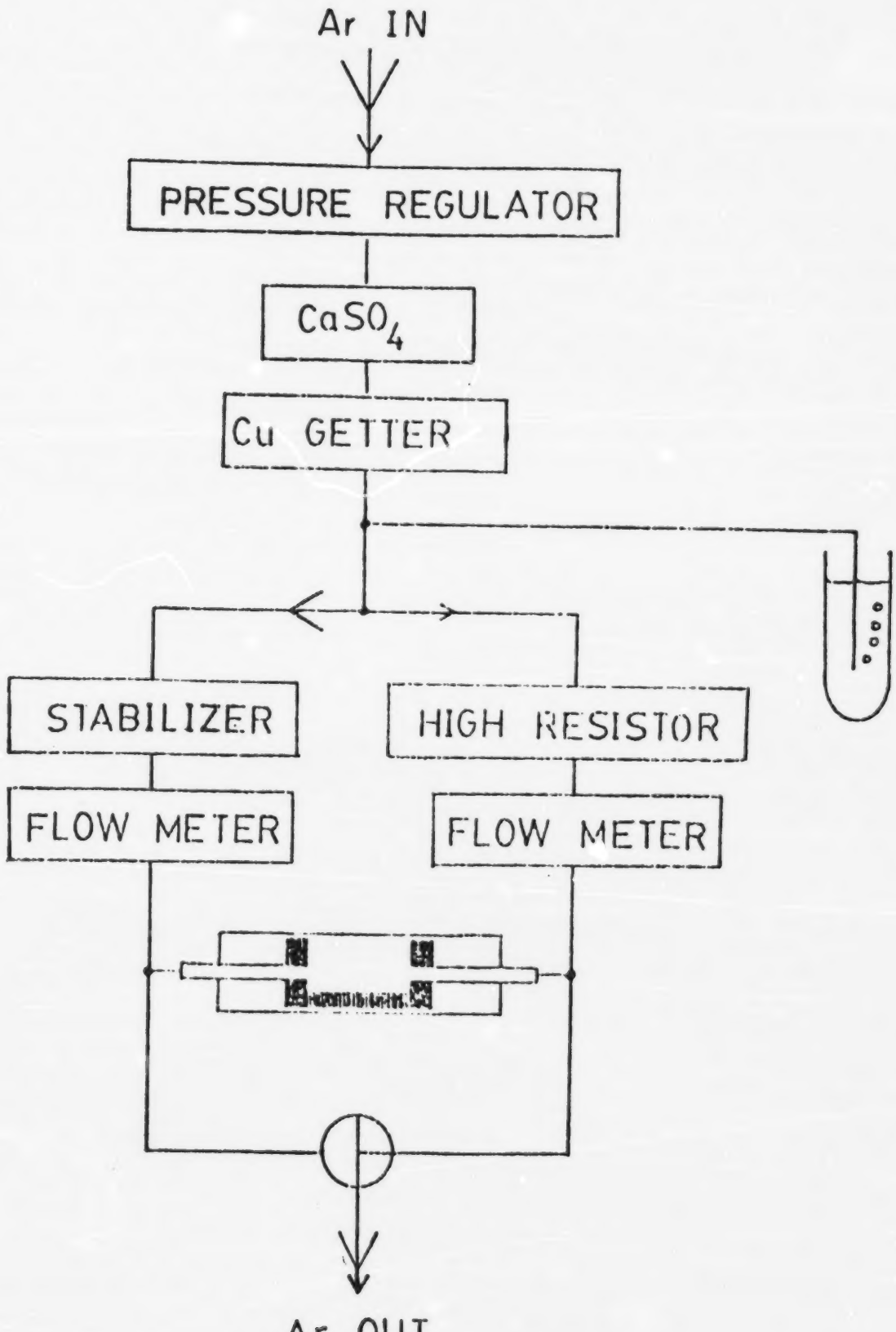

FIGURE 5. THE SCHEMATIC OF THE GAS TRAIN. THE SYSTEM IS SHOWN IN THE FORWARD CYCLE.

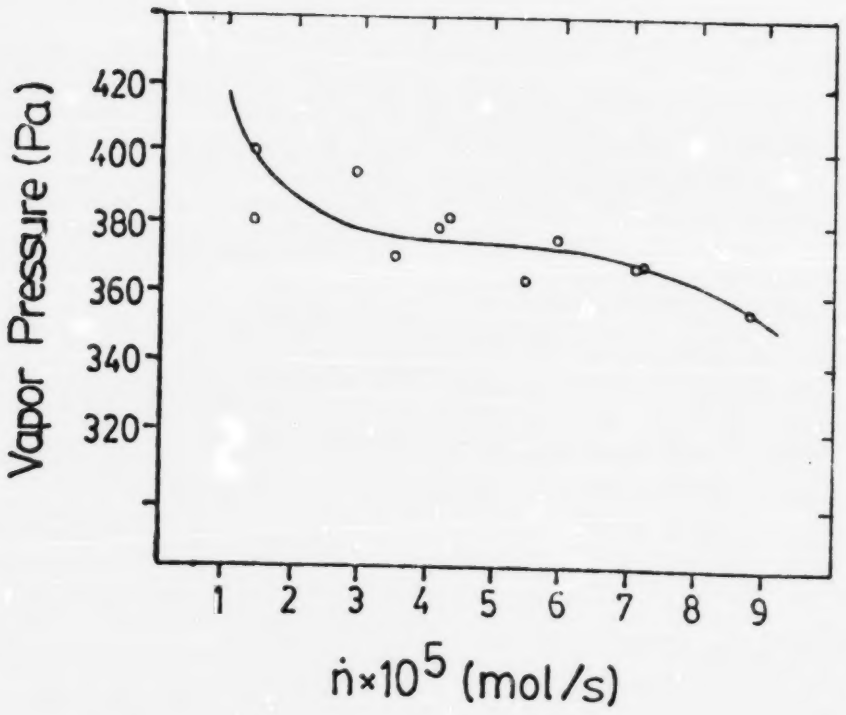

FIGURE 6. THE SATURATION CURVE FOR As_4C_6

In Fig. 7 and Table III, the results of 5 temperatures are summarized. The very small temperature range of 50°C did not justify the derivation of the enthapy terms. However, as shown in Fig. 7, good agreement is obtained with the recommended literature value.

Table III

Temperature		Pressure	
K	$1/T \times 10^3$	Pa	logPatm
493	2.028	373.6	-2.4337
503	1.988	706.6	-2.1565
523	1.912	1733	-1.7669
533	1.876	2453	-1.6160
543	1.842	3746	-1.4321

Conclusion

The vapor pressure of As_4O_6 over a temperature range of 220 to 270°C was determined to check the reliability of the transportation apparatus. Good agreement was obtained with the recommended literature value.

Future Work

It is recommended that this transportation cell assembly be combined with a high temperature reactor to study the thermodynamics of complex arsenates.

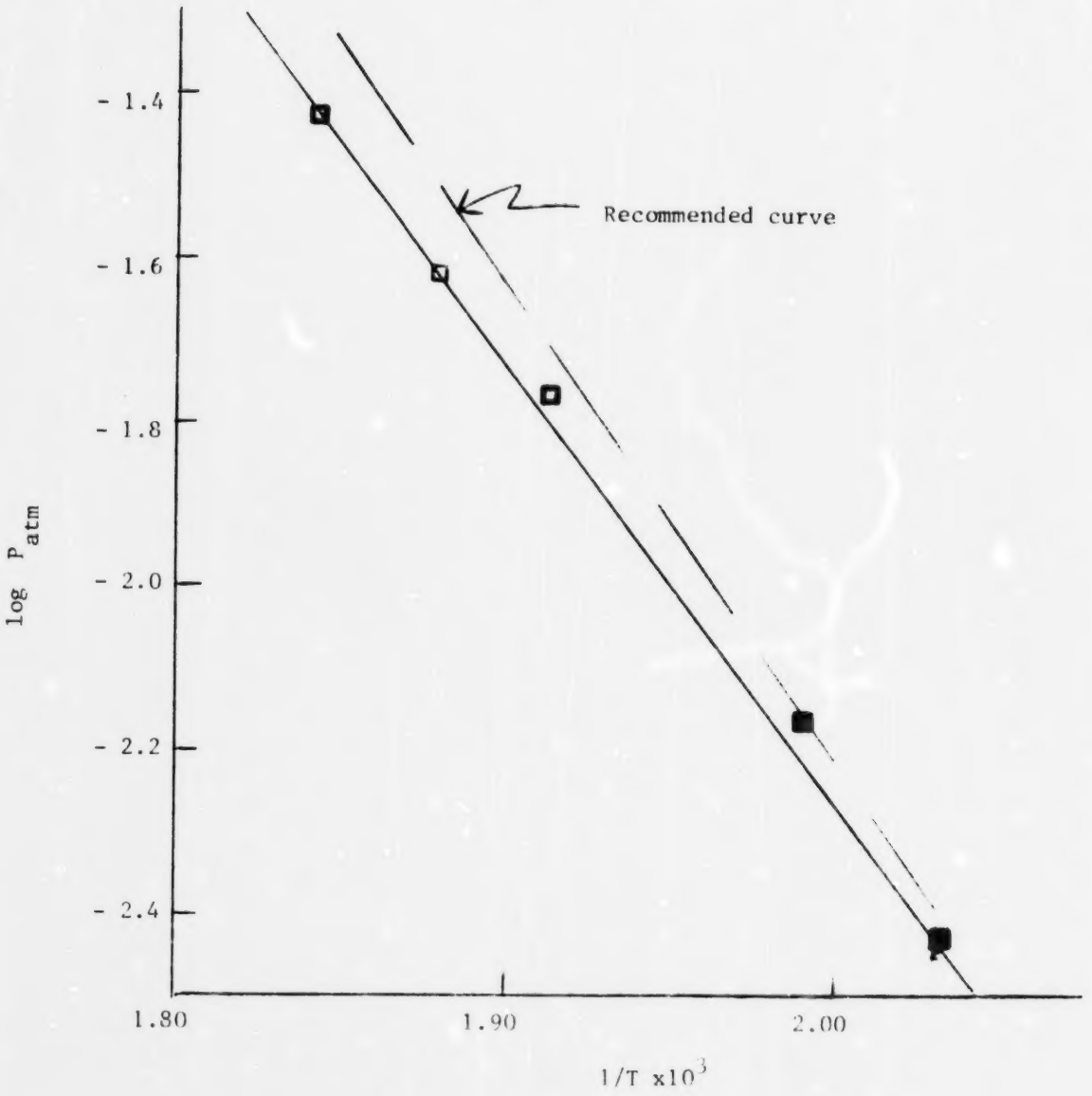

FIGURE 7. VAPOR PRESSURE OF As_4O_6 .

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PART III

THERMODYNAMIC DATA

Table 1 Dissociation reactions and temperature of each synthesized compound in Ar atmosphere (7).

Dissociation reaction	Diss. temp.(°C)
$3Ag_2O \cdot As_2O_3(s) = 6Ag(s) + 1/2As_4O_6(g) + 3/2O_2(g)$ ····· (1)	200
$3CaO \cdot As_2O_3(s) = 3CaO(s) + 1/2As_4O_6(g)$ ····· (2)	730
$Fe_2O_3 \cdot As_2O_3(am) = Fe_2O_3(s) + 1/2As_4O_6(g)$ ····· (3)	350
$Al_2O_3 \cdot As_2O_5(s) = Al_2O_3(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (4)	800
$2\{CaO \cdot As_2O_5(s)\} = 2CaO \cdot As_2O_5(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (5)	750
$3\{2CaO \cdot As_2O_5(s)\} = 2\{3CaO \cdot As_2O_5(s)\} + 1/2As_4O_6(g) + O_2(g)$ ···· (6)	1050
$3CaO \cdot As_2O_5(s) = 3CaO(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (7)	1400
$2\{CoO \cdot As_2O_5(s)\} = 2CoO \cdot As_2O_5(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (8)	630
$3\{2CoO \cdot As_2O_5(s)\} = 2\{3CoO \cdot As_2O_5(s)\} + 1/2As_4O_6(g) + O_2(g)$ ···· (9)	860
$3CoO \cdot As_2O_5(s) = 3CoO(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (10)	1060
$Cr_2O_3 \cdot As_2O_5(s) = Cr_2O_3(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (11)	860
$3\{2CuO \cdot As_2O_5(s)\} = 2\{3CuO \cdot As_2O_5(s)\} + 1/2As_4O_6(g) + O_2(g)$ ···· (12)	800
$Fe_2O_3 \cdot As_2O_5(s) = Fe_2O_3(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (13)	850
$3MgO \cdot As_2O_5(s) = 3MgO(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (14)	1270
$3\{2NiO \cdot As_2O_5(s)\} = 2\{3NiO \cdot As_2O_5(s)\} + 1/2As_4O_6(g) + O_2(g)$ ···· (15)	650
$3NiO \cdot As_2O_5(s) = 3NiO(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (16)	930
$2TiO_2 \cdot As_2O_5(s) = 2TiO_2(s) + 1/2As_4O_6(g) + O_2(g)$ ····· (17)	800
$4CoAsS(s) = 4CoS(s) + As_4(g)$ ····· (18)	450
$4FeAsS(s) = 4FeS(s) + As_4(g)$ ····· (19)	500
$4NiAsS(s) = 4NiS(s) + As_4(g)$ ····· (20)	450

(am):amorphous,(s):solid,(g):gas

Table 2 The values of A and B in the equation of $\log K = -A/T + B$, where K is the equilibrium constant of the dissociation reactions shown in Table 1 (7).

Compound	-A	B	temp.range(°c)
$3Ag_2O \cdot As_2O_3$(s)	10960(±20)	16.95(±0.03)	227°-298°
$Fe_2O_3 \cdot As_2O_3$(am)	2790(±6)	2.94(±0.01)	325°-425°
$3CaO \cdot As_2O_3$(s)	5820(±10)	4.03(±0.01)	811°-891°
$Al_2O_3 \cdot As_2O_5$(s)	23800(±30)	17.47(±0.01)	786°-915°
$CaO \cdot As_2O_5$(s)	23480(±80)	16.34(±0.06)	905°-988°
$2CaO \cdot As_2O_5$(s)	26950(±50)	16.47(±0.03)	1017°-1115°
$CoO \cdot As_2O_5$(s)	18620(±35)	15.61(±0.03)	608°-779°
$2CoO \cdot As_2O_5$(s)	21070(±35)	14.13(±0.03)	870°-977°
$3CoO \cdot As_2O_5$(s)	28050(±80)	17.88(±0.05)	979°-1108°
$Cr_2O_3 \cdot As_2O_5$(s)	25190(±35)	18.67(±0.03)	801°-905°
$2CuO \cdot As_2O_5$(s)	21270(±25)	16.02(±0.02)	725°-826°
$Fe_2O_3 \cdot As_2O_5$(s)	24130(±10)	17.44(±0.01)	785°-910°
$2NiO \cdot As_2O_5$(s)	19980(±140)	15.97(±0.14)	670°-802°
$3NiO \cdot As_2O_5$(s)	25320(±80)	16.38(±0.06)	948°-1057°
$2TiO_2 \cdot As_2O_5$(s)	21450(±15)	16.61(±0.01)	751°-850°

Table 3 ΔG° for the formation reaction of one mole of arsenate formed from a half mole of As_4O_6 gas and one mole of O_2 gas as a function of 1/T and ΔG°_{298} estimated from ΔG° (7).

	ΔG° (cal/mol)	$\Delta G^\circ_{(298)}$ (kcal/mol)
As_2O_5	$\Delta G^\circ = -68801.1(\pm 25) + 66.12(\pm 0.05)T$	-49.1
$Al_2O_3 \cdot As_2O_5$	$\Delta G^\circ = -54490.5(\pm 3) + 39.97(\pm 0.05)T$	-42.6
$CaO \cdot As_2O_5$	$\Delta G^\circ = -139313.3(\pm 320) + 76.65(\pm 0.3)T$	-116.5
$2CaO \cdot As_2O_5$	$\Delta G^\circ = -171228.5(\pm 20) + 76.45(\pm 0.2)T$	-148.4
$3CaO \cdot As_2O_5$	$\Delta G^\circ = -195210.7(\pm 50) + 77.0(\pm 0.3)T$	-172.3
$CoO \cdot As_2O_5$	$\Delta G^\circ = -101438.6(\pm 203) + 73.75(\pm 0.2)T$	-79.5
$2CoO \cdot As_2O_5$	$\Delta G^\circ = -117681.2(\pm 264) + 76.08(\pm 0.2)T$	-95.0
$3CoO \cdot As_2O_5$	$\Delta G^\circ = -128333.3(\pm 321) + 81.80(\pm 0.2)T$	-104.0
$Cr_2O_3 \cdot As_2O_5$	$\Delta G^\circ = -57626.7(\pm 74) + 42.71(\pm 0.07)T$	-44.9
$Fe_2O_3 \cdot As_2O_5$	$\Delta G^\circ = -55202.0(\pm 5) + 39.89(\pm 0.03)T$	-43.3
$3MgO \cdot As_2O_5$	$\Delta G^\circ = -163743.8(\pm 97) + 78.32(\pm 0.1)T$	-140.4
$2NiO \cdot As_2O_5$	$\Delta G^\circ = -107700.1(\pm 435) + 74.31(\pm 0.42)T$	-85.6
$3NiO \cdot As_2O_5$	$\Delta G^\circ = -115852.7(\pm 350) + 74.94(\pm 0.3)T$	-93.5
$2TiO_2 \cdot As_2O_5$	$\Delta G^\circ = -98129.2(\pm 50) + 76.0(\pm 0.05)T$	-75.5

Table 4. ΔG°_{T} for the species and compounds of arsenic. (8).

reaction	temperature range (K)	$\Delta G^{\circ} = A + B\,T$ (cal) A	B
$As(s) = As(l)$	1089	5,650	-5.19
$As(s) = As(g)$	298 - 800	71,640	-32.07
$As(s) = 1/2As_2(g)$	298 - 800	22,050	-18.51
$As(s) = 1/3As_3(g)$	298 - 800	18,350	-11.80
$As(s) = 1/4As_4(g)$	298 - 800	8,800	-9.94
$As(s) + 3/4O_2(g) = 1/2As_2O_3(l)$	582 - 734	-74,140	23.19
$As(s) + 5/4O_2(g) = 1/2As_2O_5(s)$	298 - 600	-104,870	48.71
$1/2As_2(g) + 1/2O_2(g) = AsO(g)$	298 -1500	-6,990	-3.19
$1/2As_2(g) + 3/4O_2(g) = 1/4As_4O_6(g)$	298 - 876	-93,340	39.06
$As(s) + 1/2S_2(g) = 1/2As_2S_2(l)$	580 - 700	-30,730	17.54
$As(s) + 3/4S_2(g) = 1/2As_2S_3(l)$	585 - 800	-37,970	20.80
$1/2As_2(g) + 1/2S_2(g) = AsS(g)$	298 -1200	10,340	0.33
$1/2As_2(g) + 1/2S_2(g) = 1/4As_4S_4(g)$	298 -2000	-36,710	26.63
$As(s) + Fe(s) + 1/2S_2(g) = FeAsS(s)$	773 - 975	-40,490	16.30
$As(s) + Ni(s) + 1/2S_2(g) = NiAsS(s)$	723 - 973	-20,120	3.13
$1/2As_2(g) + 3/2H_2(g) = AsH_3(g)$	298 -1200	-8,330	25.34
$1/2As_2(g) + 3/2F_2(g) = AsF_3(g)$	330 -1000	-242,150	30.88
$1/2As_2(g) + 5/2F_2(g) = AsF_5(g)$	298 -1200	-315,850	69.94
$1/2As_2(g) + 3/2Cl_2(g) = AsCl_3(g)$	308 -1000	-86,400	28.43
$1/2As_2(g) + 3/2Br_2(g) = AsBr_3(g)$	298 -1100	-64,250	27.50
$As(s) + 3/2I_2(g) = AsI_3(l)$	414 - 644	-30,400	33.02
$As(s) + 1/2Fe(s) = 1/2FeAs_2(s)$	773 -1123	-5,180	-3.58
$As(s) + Fe(s) = FeAs(s)$	673 -1073	-4,170	-8.34
$As(s) + 2Fe(s) = Fe_2As(s)$	673 -1073	-1,110	-13.01
$As(s) + Ni(s) = NiAs(s)$	298 - 800	-17,530	4.14
$As(s) + 3Cu(s) = Cu_3As(s)$	298 -1098	-25,920	0.33
$As(s) + 3Na(l) = Na_3As(s)$	371 - 800	-54,540	19.06

Table 5 Heats of reaction and dissociation temperatures of arsenates. (8).

	ΔH°_{298} (kcal)	T_d (K)		ΔH°_{298} (kcal)	T_d (K)
$K_6(AsO_4)_2$	-254.5	4683	$Co_3(AsO_4)_2$	-42.8	1622
$Na_6(AsO_4)_2$	-220.2	4185	$Cd_3(AsO_4)_2$	-39.2	1571
$Li_6(AsO_4)_2$	-128.8	2865	$Fe_3(AsO_4)_2$	-36.8	1536
$Ba_3(AsO_4)_2$	-141.8	3054	$Zn_3(AsO_4)_2$	-23.9	1350
$Sr_3(AsO_4)_2$	-113.5	2644	$Mn_2(AsO_4)_2$	-16.7	1246
$Ca_3(AsO_4)_2$	-78.9	2144	$Cu_3(AsO_4)_2$	-11.7	1173
$Mg_3(AsO_4)_2$	-40.4	1588	$Al_2(AsO_4)_2$	-10.8	1160
$Pb_3(AsO_4)_2$	-46.4	1674	$Fe_2(AsO_4)_2$	-10.5	1156
$Ag_6(AsO_4)_2$	-42.8	1622			

Table 6 Standard free energy change for formations $\Delta G^{\circ}_{f,298}$ (kcal/mol). (8)

arsenic species	state	ΔG°
AsO^{+}	(aq)	-39.15
$HAsO_2$	(aq)	-96.25
AsO_2^{-}	(aq)	-83.66
H_3AsO_4	(aq)	-183.1
$H_2AsO_4^{-}$	(aq)	-180.04
$HAsO_4^{2-}$	(aq)	-170.82
AsO_4^{3-}	(aq)	-155.00
AsH_3	(g)	+16.47
arsenic oxide		
As_2O_3	(c)	-137.72
As_2O_5	(c)	-187.0
arsenic sulfide ion		
AsS_2^{-}	(aq)	-11.3
$As_3S_6^{3-}$	(aq)	-60.32
arsenic sulfide		
As_2S_2	(c)	-33.4
As_2S_3	(c)	-40.3
FeAsS	(c)	-12.
metal arsenide		
AlAs	(c)	-29.0
GaAs	(c)	-16.2
InAs	(c)	-12.8
Zn_3As_2	(c)	-30.0
Cd_3As_2	(c)	-7.7
Cu_3As	(c)	-25.8
Ni_5As_2	(c)	-38.34
$Ni_{11}As_8$	(c)	-113.92
NiAs	(c)	-11.99
$NiAs_2$	(c)	-15.45
Co_2As	(c)	-27.39
CoAs	(c)	-15.77
$CoAs_2$	(c)	-19.46
$CoAs_3$	(c)	-19.46
Fe_2As	(c)	-43.2
FeAs	(c)	-30.1
$FeAs_2$	(c)	-42:4
MnAs	(c)	-13.7
UAs_3	(c)	-173.
Na_3As	(c)	-44.8
NaAs	(c)	-21.3
$NaAs_2$	(c)	-24.8
metal arsenite		
$Zn(AsO_2)_2$	(c)	-219.6
$3ZnO \cdot As_2O_3$	(c)	-375.8
$Cu(AsO_2)_2$	(c)	-167.7
$Ca(AsO_2)_2$	(c)	-308.8
$CaAsO_2OH$	(c)	-266.0
$Sr(AsO_2)_2$	(c)	-307.5
$SrAsO_2OH$	(c)	-262 4
$BaH(AsO_2)_3$	(c)	-406.6
$Ba(AsO_2)_2$	(c)	-307.2
$Ba_2(AsO_2)_3OH$	(c)	-570.2
$Ba_5(AsO_2)_6(OH)_4$	(c)	-1354.7
metal arsenate		
$SbAsO_4$	(c)	-176.2
$BiAsO_4$	(c)	-148.0*
$Pb_3(AsO_4)_2$	(c)	-375.8*
$AlAsO_4$	(c)	-292.6*
$ZnHAsO_4$	(c)	-214.8
$Zn_5H_2(AsO_4)_4$	(c)	-886.5
$Zn_3(AsO_4)_2$	(c)	-455.2

(Table 7 continued)

	state	ΔG°		state	ΔG°
Zn_2AsO_4OH	(c)	-297.9	$CrAsO_4$	(c)	-233.9*
$Cd_3(AsO_4)_2$	(c)	-410.2*	$MgHAsO_4$	(c)	-283.8
Hg_3AsO_4	(c)	-139.1*	$Mg_3(AsO_4)_2$	(c)	-663.3
$CuHAsO_4$	(c)	-164.8	$Ca(H_2AsO_4)_2$	(c)	-490.9
$Cu_5H_2(AsO_4)_4$	(c)	-636.9	$CaHAsO_4$	(c)	-307.7
$Cu_3(AsO_4)_2$	(c)	-310.9*	$Ca_5H_2(AsO_4)_4$	(c)	-1347.2
Cu_2AsO_4OH	(c)	-201.3	$Ca_3(AsO_4)_2$	(c)	-731.5
Ag_3AsO_4	(c)	-129.7*	Ca_2AsO_4OH	(c)	-475.1
$NiHAsO_4$	(c)	-188.4	$SrHAsO_4$	(c)	-308.8
$Ni_3(AsO_4)_2$	(c)	-379.2	$Sr_3(AsO_4)_2$	(c)	-732.3
$CoHAsO_4$	(c)	-192.2	$Sr_7(AsO_4)_4(OH)_2$	(c)	-1687.9
$Co_3(AsO_4)_2$	(c)	-338.3	$Ba(H_2AsO_4)_2$	(c)	-494.7
$FeAsO_4$	(c)	-185.0	$BaHAsO_4$	(c)	-311.8
$Mn_3(AsO_4)_2$	(c)	-512.7*	$Ba_3(AsO_4)_2$	(c)	-735.4

*estimated from Chukhlantsev's work (22, 23)

$\Delta G^\circ_{f,\ 298}$ (cal/mol) for other metal arsenates

	state	ΔG°_f		state	ΔG°_f
Li_3AsO_4	(c)	-381.49	$GaAsO_4$	(c)	-215.47
Na_3AsO_4	(c)	-357.76	$YAsO_4$	(c)	-338.47
K_3AsO_4	(c)	-370.46	$InAsO_4$	(c)	-209.40
Cu_3AsO_4	(c)	-149.17	$LaAsO_4$	(c)	-347.94
Rb_3AsO_4	(c)	-371.36	Tl_3AsO_4	(c)	-202.57
Cs_3AsO_4	(c)	-369.54	$Cr_3(AsO_4)_2$	(c)	-484.54
Au_3AsO_4	(c)	-71.17	$MoAsO_4$	(c)	-195.51
$Be_3(AsO_4)_2$	(c)	-603.69	$ReAsO_4$	(c)	-161.82
$Hg_3(AsO_4)_2$	(c)	-246.81	$Fe_3(AsO_4)_2$	(c)	-422.21
$Ra_3(AsO_4)_2$	(c)	-741.84	$Sn_3(AsO_4)_2$	(c)	-374.01
$ScAsO_4$	(c)	-319.50	$Ti_3(AsO_4)_2$	(c)	-379.8

TABLE 8

Thermodynamic Values for Arsenic Vapour Selected for Use in this Study ((9)

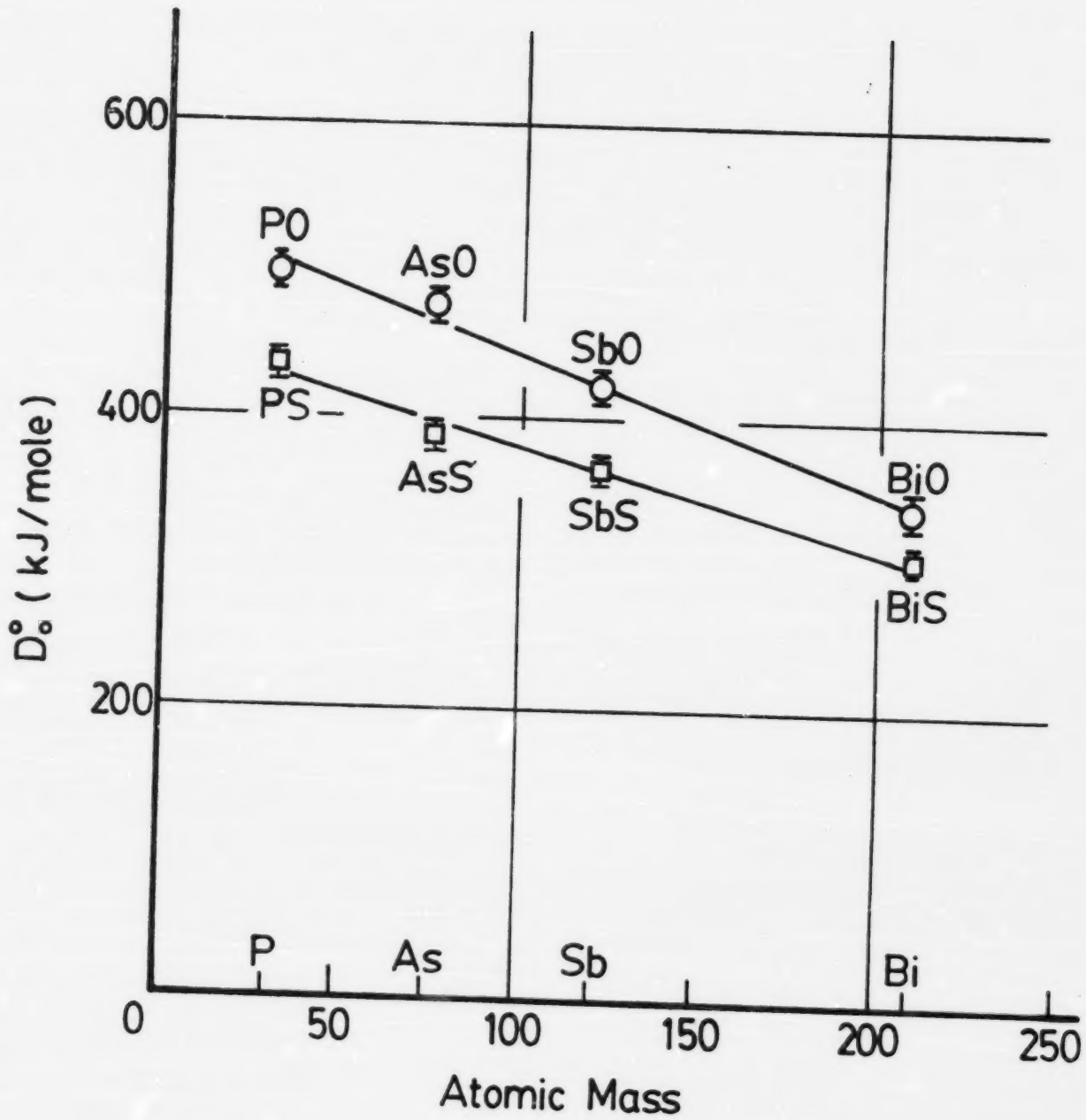
Reaction	ΔH°_{298} (kJ)
$As_4(g) = 2As_2(g)$	227.0 ± 2.9
$\frac{1}{2}\ As_2(g) = As(g)$	191.3 ± 1.1
$\frac{1}{3}\ As_3(g) = \frac{1}{3}\ As_2(g) + \frac{1}{3}\ As(g)$	87.1 ± 9.6
$4As(s) = As_4(g)$	156.2 ± 2.4

Heats of Formation

Species	ΔH°_f (298 K) kJ mol^{-1}
As(g)	287.1
$As_2(g)$	191.6
$As_3(g)$	217.4
$As_4(g)$	156.2

Equilibrium Constants for Arsenic Vapour Dissociation

Reaction	log K
$\frac{1}{4}\ As_4(g) \rightleftharpoons As(g)$	$4.846 - \frac{13770}{T}$
$\frac{1}{2}\ As_4(g) \rightleftharpoons As_2(g)$	$3.882 - \frac{5879.8}{T}$
$\frac{3}{4}\ As_4(g) \rightleftharpoons As_3(g)$	$3.394 - \frac{7652.2}{T}$



Dissociation energies at 0 K, D^0_0 kJ/mol, for diatomic oxide and sulfide gases.(10)

APPENDIX I

Thermodynamics: Arsenic and Arsenic Oxides

84: 126111q Trace element behavior in coal-fired power plant. Kaakinen, John W.; Jorden, Roger M.; Lawasani, Mohammed H.; West, Ronald E. (Dep. Chem. Eng., Univ. Colorado, Boulder, Colo.). *Environ. Sci. Technol.* 1975, 9(9), 862-9 (Eng). Measurements of the amts. of 17 elements in the inlets and outlets of a pulverized-coal-fired power plant indicate that Al, Fe, Rb, Sr, Y, and Nb were at essentially const. concns. in all outlet ashes, and that concns. of Cu, Zn, As, Mo, Sb, Pb, ^{210}Po, and Se were generally lowest in bottom ash and increased progressively in fly ashes collected downstream toward the stack. A model was developed for the enrichment behavior in downstream ashes of this latter group of elements assuming that these elements vaporize in the furnace and then condense or absorb onto fly ash; smaller particles have larger specific surface areas and thus will have greater concns. of these elements, and an increase proportion of smaller particles in downstream fly ashes results in enrichment of these elements. Exptl. enrichment values for Zn, As, Mo, and Sb agree with values predicted by this model.

84: 121032c Thermodynamic studies of the arsenic triple point. Baker, E. H. (Nuffield Res. Group Extr. Metall., Imp. Coll., London, Engl.). *Inst. Min. Metall., Trans., Sect. C* 1974, 83(Dec.), C237-C240 (Eng). The sublimation, fusion, and liq.-vapor relations were studied for As [7440-38-2] in the triple-point region by DTA and calorimetrically using an internally heated pressure vessel. The triple-point parameters are 816° and 35.5 atm. The heat of fusion was detd. to be 5720 cal/g atom from the vapor pressure data and 6600 ± 200 cal/g atom by DTA; the latter value is more reliable.

83: 126294f Kinetics and thermodynamics of sublimation [of] antimony. Gerd M. (Pennsylvania State Univ., University Park, Pa.). *U. S. NTIS, AD-A Rep.* 1975, No. 0084/3, 40 pp. (Eng). Avail. NTIS. *From Gov. Rep. Announce. Index (U. S.)* 1975, 75(12), 65. Measurements were made of the rate of vaporization of As and Sb single crystals under varied conditions. Measurements were also made of reaction rates with O_2, changes in surface morphol. accompanying sublimation of As, NaCl, KCl, and other substances were followed in order to elucidate the vaporization mechanism of these solids which have low vaporization coeffs. A "zipper" mechanism appears to describe the vaporization of As. Ultra high vacuum studies of condensation and crystal growth were carried out on As. A method and app. were developed to det. translational and internal energy accommodation coeffs. Thermodn. properties of the As, As-O, Sb-Sb-O, and Se-O systems were detd.

83: 149769d Arsenic and antimony additives in unseeded and potassium-seeded hydrogen/oxygen flames. Farber, Milton; Srivastava, R. D. (Space Sci., Inc., Monrovia, Calif.). *Combust. Flame* 1975, 25(1), 101-6 (Eng). The reactions with As [7440-38-2] and Sb [7440-36-0] additives in H_2 [1333-74-0]/O_2 flames and H_2/O_2 flames seeded with K [7440-09-7] were studied. The flame was atm. and a mol. beam of the frozen species was introduced into the mass spectrometer through a 2-stage differential pumping system operating from 1 to 10^{-6} atm. As compds. found in the flame included AsO [12005-99-1](g), $HAsO_2$ [13002-53-1](g) and H_3AsO_4 [7778-39-4](g). Heat of formation values, ΔH_{f298}, were calcd. as -145.4±5 for $HAsO_2$(g) and -250.7±5 kcal-mole for H_3AsO_4(g). Sb compds. included SbO(g), SbO [12281-27-5](g), $HSbO_2$ [13473-74-0](g) and H_3SbO_4 [13453-10-6](g), yielding ΔH_{f298} values of 18.7±5 kcal/mole for SbO(g), -137.4±5 for $HSbO_2$(g), and -262.9±5 for H_3SbO_4(g). The formation of the K compds. KH_2AsO_4 [7784-41-0](g) and KH_2SbO_4 [15478-80-5](g) was also established. Heat of formation values, ΔH_{f298} obtained for the K-substituted compds. were -299.5±5 and -303.7±5 kcal/mole for KH_2AsO_4(g) and KH_2SbO_4(g), resp.

82: 145432y Equilibrium vapor concentrations of some polycyclic aromatic hydrocarbons, arsenic oxide (As_2O_3), and selenium dioxide. Comments. Pupp, Christian; Lao, Robert C.; Murray, John J.; Pottie Roswell F. (Environ. Health Cent., Dep. Environ., Ottawa, Ont.). *Atmos. Environ.* 1975, 9(3), 367 (Eng). Corrections to a previous paper (C. Pupp et al. *Atmospheric Environment*, 1974, 8, 915) are given.

82: 10392Sf Vapor composition and van der Waals constants of arsenic. Rau, Hans (Philips Forschungslab. Aachen G.m.b.H., Aachen, Ger.). *J. Chem. Thermodyn.* 1975, 7(1), 27-32 (Eng). Std. enthalpies of formation and van der Waals consts. of As_2(g) [12187-08-5] and As_3(g) [23378-46-8] were derived from vapor pressure and d. measurements up to 77 atm and ~1400°K. The following results were obtained: ΔH_f°(As_2, g, 298.15°K) = (37.34 ± 0.2) kcal mole^{-1}; ΔH_f°(As_3, g, 298.15°K) = (45.54 ± 0.5) kcal mole^{-1}; $a = 7.12 \times 10^5$ atm cm^6 mole^{-2}; $b = 349.1$ cm^3 mole^{-1}.

82: 62412n Adsorption of arsenic(III) oxide vapors. Terebenin, A. N.; Bykov, A. P.; Meshkova, V. S. (USSR). *Tsvetn. Met.* 1974, (9), 21-3 (Russ). The adsorption of As_2O_3 vapor on Fe_2O_3, CaO, ZnO, and SnO_2 at 200-1000° was studied with respect to the contamination of fuming dusts of Sn metallurgy. Adsorption on Fe_2O_3, CaO, and ZnO was max. at 600-800°, and was accompanied by a marked oxidn. to As_2O_5. Decreasing the gaseous O concn. decreased the As_2O_3 adsorption. The chief component of the fume, SnO_2, sorbed As_2O_3 but little. The prevention of contamination of the sublimates by As_2O_3 is discussed. E. M. Elkin

81: 175309g Equilibrium vapor concentrations of some polycyclic aromatic hydrocarbons, arsenic trioxide (As_2O_3) and selenium dioxide, and the collection efficiencies of these air pollutants. Pupp, Christian; Lao, Robert C.; Murray, John J.; Pottie, Roswell F. (Air Pollut. Control Directorate, Dep. Environ., Ottawa, Ont.). *Atmos. Environ.* 1974, 8(9), 915-25 (Eng). The satd. or equil. vapor concns. of the following inorg. substances and polycyclic arom. hydrocarbons are reported. SeO_2, As_2O_3, pyrene, benz[a]anthracene (I), benzo[e]pyrene (II), benzo[a]pyrene (III), benzo[k]fluoranthene (IV), benzo[ghi]perylene (V), and coronene. The significance of these results with respect to the efficacy of collection of these pollutants on particulate filters and the validity of the previous measurements of collection efficiency are considered. Significant losses may be expected for some of these compds. (As_2O_3, SeO_2, pyrene, and I, that the efficacy of collection is subject to considerable question for some others (II, III, IV), although losses may be minimized by adsorption effects, and that for others, (V, coronene) losses should be insignificant.

83: 85936j Vaporization of arsenic and zinc from cadmium melts. Ivanov, Yu. M.; Kaller, Ya. A. (USSR). *Khal'kogenidy Tsinka, Kadmiya Rtuti* 1973, 57-61 (Russ). From *Ref. Zh., Met.* 1973, Abstr. No. 5G359. Vapor compn. over a Cd-Zn-As melt was detd. by mass spectrometry, and the Cd to impurity ratio was calcd. As and Zn were eliminated from Cd by low-temp. vacuum distn.

83: 77915q Fractional sublimation purification and coulometric assay of arsenic trioxide. Saito, Shinichi; Tanaka, Tatsuhiko; Yoshimori, Takayoshi (Sophia Univ., Tokyo, Japan). *Bunseki Kagaku* 1973, 22(11), 1460-5 (Japan). As_2O_3 was purified by fractional sublimation with both horizontal and vertical types of app. by using thermal gradients of 1.5-3°C/cm and 10-12°C/cm, resp., by heating the sample at 110° and 210°, resp., for 8-10 hr and 30 min, resp., under 2.5×10^{-3} mm Hg. Cryst. As_2O_3 obtained was 100.03% pure, as detd. by coulometric titrn., and can be used as std. reagent for titrimetric anal. H. Wada

77:102573s Knudsen-method study of the saturated vapor pressure of substances with a slow establishment of vapor-solid equilibrium. Kazhlaeva, R. I.; Shakhtakhtinskii, M. G. (Fiz. Inst., Baku, USSR). *Izv. Akad. Nauk Azerb. SSR, Ser. Fiz.-Tekh. Mat. Nauk* 1972, (2), 52–5 (Russ). A modified Knudsen method is described for the study of the satd. vapor pressure (p) in a system slowly achieving vapor-solid equil. The method was tested on As. The empirically developed equation for calcg. the dependence of the As pressure on temp. (T) is: $\log p = 10.454 - 7057.62/T$. The heat of As sublimation is 32 kcal/g-atom.

77:489046e Arsenic vapor pressure and vapor phase composition. Mamedov, A. N.; Gadzhiev, S. M.; Kuliev, A. A. (USSR). *Uch. Zap., Azerb. Unta., Ser. Khim.* 1971, No. 2, 69–73 (Russ). From *Ref. Zh., Khim.* 1972, Abstr. No. 6B802. The As vapor pressures were measured at 630–1270°K by using a membrane null manometer. The calcd. heat of sublimation is 30.1 kcal/g atom (630–830°K). The dissocn. of As_4 mols. started at >850°K (1) $As_4 = 2As_2$ (equil. const. K_p). Partial pressures of As_4 and As_2 and the temp. dependence of K_p were calcd. at 881–1263°K: $\log K_p$ (mm) = $-11800/T + 11.8$. Enthalpy and entropy change of the reaction (1) are 53.9 kcal/mole and 54.0 cal/g atom, resp.

77:155600f Deactivation processes during the forced condensation of arsenolite [cubic arsenic trioxide]. Becker, K. A.; Grosse, G. (Fritz-Haber-Inst., Max-Planck-Ges., Berlin-Dahlem, Ger.). *Z. Phys. Chem. (Frankfurt am Main)* 1972, 79(5-6), 269–77 (Ger). The distribution of the layer thickness of the product of the forced condensation of arsenolite was detd. using the γ-rays of radioactive ^{76}As. For low vapor pressure ($\sim 10^{-4}$ torr), deactivation occurs by way of an equil. between preactivated and crit. activated particles. Friedrich Epstein

77:107185g In-cavity laser Raman spectroscopy of As, and As_4O_6 vapors and the entropy of vaporization of arsenic. Baumbach, Stephen B. (Pennsylvania State Univ., University Park, Pa.). 1971, 119 pp. (Eng). Avail. Univ. Microfilms, Ann Arbor, Mich., Order No. 72-13,522. From *Diss. Abstr. Int. B* 1972, 32(11), 6263–9.

77:38724s Arsenic emissions at the Novaky power plant. Kriz, M.; Vejvoda, J. (Ustav Vyzk. Vyuziti Paliv, Bechovice, Czech.). *Sb. Pr. UVP (Ustav Vyzk. Vyuziti Paliv)* 1971, No. 24, 52–92 (Czech). A study of environmental problems assocd. with fossil fuel power plants situated along the Upper Nitra River which plants rely for fuel on 3 coals contg. As 0.08–0.4 and S 1.4–2.1%. The As is bound with S and Fe, probably as orpiment and löllingite, and burns to As_2O_3. The As_2O_3 reacts with CaO in the fly ash to form $Ca_3(AsO_3)_2$, which decomps. to $Ca_3(AsO_4)_2$ + As (vapor). The As oxidizes in excess O and reacts in a repetition of the cycle. The fallout in the environs of 5 sep. plants ranged 0.02–1.2 g As/m² in 24 hr. The atm. of 3 nearby towns ranged 0.008–0.053 vs 0.003 and 0.01 mg As m³ max. conc. for prolonged and peak exposures, resp. At the plant at Novaky, 50–90% of the As in the fly ash particles is chem. bound to the Ca naturally occurring in the coal. Addn. to the coal of a finely ground precursor of CaO, e.g., $CaCO_3$, either in the coal pulverizer or blown into the combustion chamber binds more of the As and some SO_2 as well was verified in plant runs adding, 0, 1.23, and 2.87% $CaCO_3$ based on the wt. of the coal. The corresponding "gaseous As" detns. were 0.74 to 0.054 and 0.03% based on As in the coal. The corresponding amts. of chem.-bound S in solid residues were 3.5, 8.3, and 10.9% expressed as percent of the S in the coal. Similar results were obtained at a 2nd plant. The As concn. in finer particles of fly ash is greater than coarser particles. A dosage of approx. 1% of $CaCO_3$ based on the wt. of coal is recommended. E. K. Holman

77:101006t Vaporization kinetics and thermodynamics in the arsenic-oxygen and antimony-oxygen systems. Behrens, Robert G. (Pennsylvania State Univ., University Park, Pa.). 1971, 218 pp. (Eng). Avail. Univ. Microfilms, Ann Arbor, Mich., Order No. 72-9437. From *Diss. Abstr. Int. B* 1972, 32(9), 5079.

76:145695j Vapor pressure and thermodynamics of octahedral arsenic trioxide (arsenolite). Behrens, Robert G.; Rosenblatt, Gerd M. (Dep. Chem., Pennsylvania State Univ., University Park, Pa.). *J. Chem. Thermodyn.* 1972, 4(2), 175–90 (Eng). Knudsen effusion expts. with a recording vacuum microbalance were performed on powd. As_2O_3 (arsenolite) at 367–429°K. The vapor pressure of arsenolite over this range is $(R/\text{cal °K}^{-1}\text{ mole}^{-1})\ln(p/\text{atm}) = -(27759 \pm 574)\text{°K}/T + (45.32 \pm 1.46)$. Third-law thermodynamic functions were approximated for solid arsenolite at >298.15°K. Third-law thermodynamic functions for $As_2O_3(g)$ were computed by using selected vibrational frequencies based upon available spectroscopic measurements on $As_2O_3(c)$, and on arsenolite powder and single crystals. A 3rd-law enthalpy of sublimation, $\Delta H°(298.15\text{°K}) = (28.13 \pm 0.20)$ kcal mole^{-1}, is obtained. The 2nd-law result is $\Delta H°(298.15\text{°K}) = (28.31 \pm 0.56)$ kcal mole^{-1}. These results are consistent with data of other authors. The agreement between 2nd-law and 3rd-law enthalpies supports the vibrational assignment used to compute the third-law functions and entropy of $As_2O_3(g)$, $S°(298.15\text{°K}) = (97.81 \pm 2.5)$ cal °K^{-1} mole^{-1}.

76:93924m Decomposition with sodium carbonate. Bock, Rudolf; Ali, Syed L. (Inst. Anorg. Chem. Kernchem., Johannes Gutenberg-Univ. Mainz, Mainz, Ger.). *Fresenius' Z. Anal. Chem.* 1972, 258(1), 12–15 (Ger). After decompn. of 18 metal oxides with Na_2CO_3 at ~1000° and dissoln. of the melt in H_2O, the metal content in the filtrate was detd. Very small particles were not retained quant. by the filter. The partition of SiO_2 between the soln. and the residue and the volatility of alkali metal halides, Na_2S, and In, Sb, Hg, Tl, and As oxides during the melting process were investigated.

76:47820b Arsenic of high purity by sublimation. Bienert, Klaus; Nordt, Egon; Lang, Winfried; Weidner, Herbert (Wacker-Chemitronic G.m.b.H.). Ger. Offen. 2,021,332 (Cl. C 22b), 16 Dec 1971, Appl. 30 Apr 1970; 8 pp. Arsenic of >99.99% purity, useful for the manuf. of GaAs semiconductors and doping of semiconductors, was made from As contg. 20–50 ppm Si by sublimation in contact with spectrally pure C or B powder in vacuo in quartz tubes at temp. gradient 0.8°/cm. Thus, As contg. 20 ppm Si was covered with spectrally pure C powder and sublimed in an evacuated quartz tube at evapn. temp. 500° and deposition temp. 400° to give As contg. 1 ppm Si.

76:18528q Dissociation of arsenic pentoxide. Polukarov, A. N.; Makhmetov, M. Zh.; Buketov, E. A. (Khim.-Metall. Inst., Karaganda, USSR). *Zh. Fiz. Khim.* 1971, 45(10), 2655 (Russ). Addnl. data are available from a depository whose address is cited in the original document. The satd. vapor pressure (p) of As_2O_5 in the reaction $As_2O_5(s) \rightleftharpoons 0.5As_4O_6(g) + O_2(g)$ was detd. by a static dew-point method at 537–740° and it was correlated by the equation $\log p(\text{torr}) = -10127/T(\text{°K}) + 12.50$. The equil. const. of the dissocn. and the reaction heat were also calcd.
Karel A. Hlovaty

75:68188w Heat capacities of cubic, monoclinic, and vitreous arsenious oxide from 5 to 360°K. Chang, S. S.; Bestul, A. B. (Inst. Mater. Res., Natl. Bur. Stand., Washington, D.C.). *J. Chem. Phys.* 1971, 55(2), 503–46 (Eng). Expt. detd. heat capacities, C_p, precise to better than 0.1%, and derived thermal data are reported for cubic and monoclinic cryst. and vitreous arsenious oxide at temperatures from 5 to 360°K. The C_p for the glass is higher than for either crystal at all temps. The C_p's for the cubic crystal are lower than those for the monoclinic between about 20 and 310°K and higher at temps. below and above this range. The C_p/T^3 for the glass is still increasing with decreasing temp. at 5°K, although C_p/T^3 for both crystals peaks a few degrees above this. The C_p's reported here for the monoclinic crystal are grossly different from those previously reported by Stranski, et al. The corresponding entropy difference between the 2 crystals at 298.15°K reported is 5.9 ± 0.2 J degree^{-1} mole^{-1}, whereas that previously reported from C_p measurements by Stranski, et al., was 14.4 J degree^{-1} mole^{-1}. Combined with a value newly obtained elsewhere for the enthalpy difference between the 2 crystals at 298.15°K, the value reported for the entropy difference yields a transition temp. between them of 311 ± 30°K, which is in the range currently cited on other bases. The C_p values reported for the cubic crystal and the glass are consistently 4–5% lower than those previously reported by Tarasov, et al., suggesting a systematic proportional effect of the magnitude in those previous values. The proportionality of C_p to T for the cubic crystal from 65 to 160°K, previously erroneously attributed to the monoclinic crystal by Tarasov on the basis of C_p data reported by Anderson, are discussed.

71:74923r True specific heats of black crystalline phosphorus and metallic arsenic in the 13–300°K. range. Paukov, I. E.; Nogteva, V. V.; Strelkov, P. G. (USSR). *Zh. Fiz. Khim.* 1969, 43(6), 1385–9 (Russ). Both samples were tested by x-ray diffraction for the absence of amorphous fractions. The heat capacity (C_p) was measured with an accuracy of 0.1% at 40–293.8°K. and <1.7% at <40°K. for P and of 0.1% at 45–289°K., 0.5% at 20–45°K., and 2% at 13.9–20°K. for As. Entropy ($S°_{298.15}$) and enthalpy ($H°_{298.15}-H°_0$) were calcd. by numerical integration of the smoothed C_p-T or $C_p/T-T$ curve. The extrapolation for T < 13°K. was made graphically. The values of C_p at 298.15°K., $S°_{298.15}$, and $H°_{298.15}-H°_0$ are for P 5.168, 5.422 ± 0.010, and 873.0 ± 1.2; for As 5.874 cal./g. atom-degree, 8.515 ± 0.015 entropy units, and 1222.3 ± 1.7 kcal./g. atom.
L. Kuca

71:41365k Oxidation of some impurities during alkali refining of lead and the entropies and heat capacities of the formed salts. Lovchikov, V. S. (Mosk. Inst. Stali Splavov, Moscow, USSR). *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.* 1969, 12(2), 56–62 (Russ). Na_2PbO_3 has an important role in refining Pb from impurities by oxidn. Te, which resists oxidn., has to be first dissolved in NaOH and then oxidized with Na_2PbO_3: $2Na_2PbO_3 + Te = Na_2TeO_3 + Na_2O + 2Pb$. Zn is removed by oxidn. with NaOH and forms Na_2ZnO_2, which has <1.1% solv.: $4Zn + 8NaOH = Na_6Zn_4O_7 + 3Na_2O + 4H_2$. The low solv. of zincate in NaOH promotes the formation of dispersed layers during desilvering of Pb. The calcd. values for $S°_{298}$ at 25° for Na_3AsO_4, Na_2SnO_3, Na_2SbO_4, Na_2PbO_3, and Na_2PbO_2 are 42.76, 29.67, 44.70, 35.97, and 34.60 cal./mole-degree, resp. Equations for calcg. sp. heats of the above Na salts and of Pb_3O_4, As_2O_5, and Sb_2O_5 were derived.
Evan N. Davidenko

71:51267b Standard thermodynamic functions of oxides of some Group V elements. Plekhotkin, V. P. (USSR). *Zh. Prikl. Khim. (Leningrad)* 1968, 41(10), 2237–9 (Russ). Values of standard heats of formation, $\Delta H°_{298}$, standard Gibbs free energies, $\Delta F°_{298}$, and standard entropies, $S°_{298}$, were calcd. for PO, P_2O_3, P_2O_4, P_2O_5, AsO, As_2O_3, SbO, Sb_2O_3, BiO, Bi_2O_3, Bi_2O_4, Bi_2O_5, and Bi_2O_6 on the assumption of linear changes of these quantities in coordinates, in which they change linearly for Sb oxides. This assumption is correct within exptl. error.
Karel A. Hlavaty

[illegible]: 31741s Mechanism of sublimation. Somorjai, Gabor A. (Lawrence Radiat. Lab., Univ. of California, Berkeley, Calif.). *Science* 1968, 162(2853), 755–60 (Eng). A review is given on the mechanisms of sublimation of single-cryst. surfaces of NaCl, Ag, Zn, As, and CaS. 31 references.
BGJN

70: 6750m Rate of vaporization of arsenic single crystals and the vaporization coefficient of arsenic. Rosenblatt, Gerd M.; Lee, Pang-Kai (Pennsylvania State Univ., University Park, Pa.). *J. Chem. Phys.* 1968, 49(7), 2995–3006 (Eng). Rates of vaporization from (111) cleavage faces of As single crystals have been measured over the range 508–580°K. with a recording vacuum microbalance. Expressing the rates as Langmuir vapor pressures (P_L), the results are $R \ln P_L(\text{atm.}) = -(43.99 \pm 1.47)/T + (37.98 \pm 2.72)$. At 550°K., $P_L = 6.60 \times 10^{-10}$ atm. Comparison with literature equil. data yields a vaporization coeff., $\alpha_v = P_L/P_s = 4.6 \times 10^{-4}$ at 550°K., which increases with temp., $\alpha_v = \exp(-10,921/RT)$. The results are consistent with a vaporization mechanism in which the slow step involves formation of As_4 mols. and occurs prior to surface diffusion and desorption. Ancillary measurements on vaporization of wrapped As crystals, powd. As, and Knudsen-effusion expts. are presented. These data and previous vaporization studies on powdered As are correlated by using the concept of effective vaporizing areas. Some implications of the results for the equil. vapor pressure of As, the interpretation of Knudsen-effusion expts., and the abs. entropy of $As_4(g)$ are discussed.
RCJQ

68:107974b Modified mass spectrometer ion source for the study of high-temperature vaporization. Vaporization of zinc, cadmium, arsenic, selenium, cadmium arsenide, and cadmium selenide. J. B. Westmore, H. Fujisaki, and A. W. Tickner (Univ. Manitoba, Winnipeg, Can.). *Advan. Chem. Ser.* No. 72, 231–44(1968)(Eng). The construction of an ion source for vaporizations at 100–400° is described. The conditions under which the vaporizations occur are analyzed and some results presented. Thermodynamic data are presented. The accommodation coeff. for the vaporization of As_4 from solid As or from Cd_3As_2 is small and also may be small for the vaporization of Se_2 from CdSe. 18 references.
RCBJ

68: 98950t Vaporization studies on arsenic. C. C. Herrick and Roy C. Feber (Los Alamos Sci. Lab., Los Alamos, N. Mex.). *J. Phys. Chem.* 72(4), 1102–10(1968)(Eng). Angular-displacement studies of the vaporization of solid As have been made to 700°K. by using cylindrical effusion cells, free-vaporizing surfaces, and an effusion cell fabricated from sintered As powder. An automated recording system was used. Arsenic samples were prepd. and handled in such a manner as to minimize the effect of impurities. Effusion pressures did not vary as the orifice diam. ranged from 0.005 to 0.040 in. From the effusion measurements, the heat of sublimation of solid As to $As_4(g)$ at 298.15°K. was found to be 38.54 ± 0.10 kcal./mole of $As_4(g)$ whereas the free-vaporization measurements gave 44.23 ± 0.3 kcal./mole. For the calcn. of these quantities, previously available thermoputed values. A comparison of pressures resulting from these measurements suggests a temp. dependence of the condensation coeff., which was confirmed by the angular displacement measurements on the As effusion cell. 34 references.
RCKG

68: 90262t Vaporization of arsenic and antimony single crystals. Kinetics of sublimation. Reaction with gaseous oxygen. Pang-Kai Lee (Pennsylvania State Univ., University Park, Pa.). *Diss. Abstr. B* 28(6), 2376(1967)(Eng). *Univ. Microfilms* (Ann Arbor, Mich.), *Order No.* 67-15,400, 206 pp.
SNDC

67: 15507c Thermodynamic data on heavy elements and compounds. James P. Coughlin (Aerojet-Gen. Corp., Sacramento, Calif.). NASA Accession No. N65-31327, Rept. No. AD 467028. Avail. CFSTI $3.00 cy. 161-8(1965)(Eng). Among the elements and compds. of interest in propellant performance are dense inerts such as Hg and Pb; dense oxidizers such as $Zr(ClO_4)_4$, As_2O_5, and NH_4IO_3; and the dense combustible fuels such as Zr, ZrH_2, Hf, and U. For nozzle construction materials, data are needed for carbides, nitrides, borides, and silicides of Ti, Zr, Hf, V, Nb, and Ta, as well as for possible corrosion products of these elements. *From Sci. Tech. Aerospace Rept.* 3(20), 3525(1965).
TCSL

Co 103181n Vapor pressures and condensation rates of polymorphous arsenic and antimony sesquioxides. E. Jungermann and K. Plieth (Freien Univ., Berlin). *Z. Phys. Chem.* (Frankfurt am Main)53(1-6), 215-28(1967)(Ger). As_2O_3 and Sb_2O_3 vapors of the corresponding polymorphous modifications were examd. with an electromagnetic balance which allows the measurement of vapor pressures and condensation rates. The vapor pressure equations conform well with literature data obtained with other methods. The values of the condensation rates show that the mols. in the vapor phase over monoclinic claudetite and rhombic valentinite, resp., are different from those over the cubic modifications arsenolite and senarmontite.
Friedrich Epstein

Low temperature heat capacity and certain thermochemical data on the sesquioxides of As and Sb. K. A. Gorgonki and V. V. Tarasov. *Tr. Mosk. Khim.-Tekhnol. Inst.* No. 49, 11-15(1965)(Russ); cf. preceding abstr. The glass and cryst. (arsenolite) forms of As_2O_3 and two cryst. forms of Sb_2O_3 (senarmontite and valentinite) were studied in an adiabatic calorimeter. Details of lab. prepn. of the materials are given. Values of C_p are given at 10° intervals from 65–300°K. The following standard enthalpies and entropies were calcd. by graphical integration and extrapolation of the data to 0°K.

		$H°_0$	$H°_{298.1} - H°_0$	$H°_{298.1}$
As_2O_3	(arsenolite)	207.0	3910	4117
As_2O_3	(glass)	243.0	4140	4383
Sb_2O_3	(senarmontite)	254.0	4250	4504
Sb_2O_3	(valentinite)	276.0	4523	4799

(all in cal./mole)

		$S°_0$	$S°_{298.1} - S°_0$	$S°_{298.1}$
As_2O_3	(arsenolite)	5.85	22.04	27.89
As_2O_3	(glass)	6.87	23.62	30.49
Sb_2O_3	(senarmontite)	7.20	24.45	31.65
Sb_2O_3	(valentinite)	7.67	26.04	33.71

(all in cal./mole-degree)

63: 30946 Harry Watts

Heats of formation and bond energies. XIV. Heat of combustion of arsenic. A. E. Beezer and C. T. Mortimer (Univ. Keele, Engl.). *J. Chem. Soc., A, Inorg., Phys., Theoret.* 1966(3), 330-2(Eng); cf. *CA* 63, 9123g. The heat of combustion of As in O was measured in a rotating bomb calorimeter charged with an aq. soln. of NaOH, when the products of combustion are Na arsenite and Na arsenate, in aq. soln. Incorporating data for the heat of redn. of Na arsenate to Na arsenite and the heat of soln. of arsenious oxide in an aq. soln. of NaOH, the value $\Delta H_f°(As_2O_3) = -160.0 \pm 3.0$ kcal./mole is obtained.
65: 11950e RCGF

Volatilities of the fission product and uranium oxides. Ray G. Bedford and Donald D. Jackson (Univ. of California, Livermore). *U.S. At. Energy Comm.* UCRL-12314, 37 pp.(1965)(Eng). The free energies of formation of oxides of the elements between at nos. 32 and 62, with the exception of Br, I, Kr, and Xe, were compiled. The equil. abundances of the gaseous oxides were calcd. at 500–2500°K. 23 references.
63: 14292b Sister Mary John Hoye

Heat capacity of metallic arsenic at low temperatures. V. V. Nogteva, I. E. Paukov, and P. G. Surelkov (Thermo-Fiz. Inst., Novosibirsk). *Fiz. Tverd. Tela* 7(8), 2330-2(1965)(Russ). Heat capacity of metallic As was measured in an adiabatic vacuum calorimeter at 13.9–289°K. At temps. 17–27°K. heat capacity is proportional to $T^{3.4}$. As temp. decreases, the exponent increases to 3.4. Abs. entropy ($S°_{298.15}$) and the difference of enthalpy between 0 and 298.15°K. ($H°_{298.15} - H_0°$) were calcd.
63: 14147g A. Libackyj

Heats of formation and bond energies. XIII. Arsenic tribromide, arsenious and arsenic oxides, and aqueous solutions of sodium arsenite and sodium arsenate. A. E. Beezer, C. T. Mortimer, and E. G. Tyler (Univ. Keele, Engl.). *J. Chem. Soc.* 1965 (Aug.), 4471-5(Eng). The heats of reaction between Br, in CCl_4, and two forms of As (α rhombohedral, cryst.) and (β, amorphous) to give As tribromide in soln. have been measured. The heat of formation, $\Delta H_f°(AsBr_3, cryst.) = -47.57 \pm 0.10$ kcal./mole, and the heat of transition, $\Delta H = +3.24 \pm 0.03$ kcal./g.-atom, for the process As(α, rhombohedral, cryst.) → As(β, amorphous) have been calculated. The heats of hydrolysis of As tribromide, arsenious oxide, and arsenic oxide in an aq. soln. of sodium hydroxide and the heat of oxidn. of a soln. of $NaAsO_2$ to Na_3AsO_4, by using liquid Br, have also been measured. The results are used to calc. the following heats of formation: $\Delta H_f°(As_2O_3$, octa., cryst.) $= -160.30 \pm 0.22$; $\Delta H_f°(As_2O_3$, cryst.) $= -222.14 \pm 0.25$; $\Delta H_f°[NaAsO_2$, in 64 NaOH, 2000 $H_2O]$ (liq.) $= -164.57 \pm 0.20$; $\Delta H_f°[Na_3AsO_4$, in 60 NaOH, 2002 $H_2O]$ (liq.) $= -382.97 \pm 0.30$ kcal./mole. The mean bond dissociation energy $D(As-O) = 77.6 \pm 0.1$ kcal./mole is calcd. for arsenious oxide. Cf. *CA* 61, 8260d. RCJR

Stability ranges of the monoclinic phases claudetite I and claudetite II. K. A. Becker, H. Karge, and I. N. Stranski (Fritz-Haber-Inst. Phys. Chem., Berlin). *Z. Physik. Chem.* (Frankfurt) 44(1/2), 1-6(1965)(Ger). The position of monoclinic claudetite II in the phase diagram of As_2O_3 was studied. From an examn. of the conditions of formation, of the convertibility of claudetite II and I, and from the detn. of the m.p. and of the soly. follows that claudetite I and II are monotropic with respect to each other and that the latter is metastable over the whole range of its existence. Influence of the carrier on the formation of claudetite. *Ibid.* 7-14. The effect of the carrier on the crystn. of claudetite was studied. Growth expts. on various carriers show that for the formation and the growth from an aq. vapor phase which is replenished from a solid arsenolite phase, an alk. carrier is necessary. This is explained by assuming that the cleavage of the arsenolite, which is necessary for the subsequent formation of claudetite, is catalyzed by an alk. boundary layer. 63: 3702e Friedrich Epstein

The thermal distillation of arsenic trioxide. Ya. I. Ivashentsev, O. K. Nikul'chikova, and Z. I. Otmokhova. *Tr. Tomskogo Gos. Univ., Ser. Khim.* 170, 150-3(1964)(Russ). The sublimation of As_2O_3 at 300–500° yields pure product, contg. less than 10^{-4}–10^{-5}% of Sb, Al, Fe, Si, Mn, Mg, Cu, Zn, Pb, Bi, Ti, Ni, Ca, and Co. The addn. of 5–20% MnO_2 prevents the distn. of Sb_2O_3 and shortens the time of As_2O_3 distn.
63: 2736 J. Palaty

Purification of arsenic by a thermal method. Ya. I. Ivashentsev and G. A. Kataev. *Tr. Tomskogo Gos. Univ., Ser. Khim.* 154, 189-92(1962). A new method of As purification consists in thermal distn. of As oxides and their redn. with graphite in a continuous process. A quartz ampul divided into 3 zones was used. In zone *A* (30 cm. long) As oxide was distd., in *B* (35 cm. long) contg. granulated graphite As oxide was reduced, and in *C* (20 cm. long) it was condensed. As_2O_3 contg. admixts. of 15 metals <0.1% was distd. at 750–800°, reduced at 850–900°, condensed at 230–320° in 60 min. with 50% yield. The product contained admixts. of Al, Sb, Cu, Mg, Co, Fe, Zn, Ni, Pb, Mn, Ti, Cr, Bi < 1×10^{-4}, of Cd < 1×10^{-3}, of Si < 1×10^{-2}%. As_2O_3 contg. admixts. of Sb <1%, and <0.1% of 14 other metals was distd. at 460–500° and 380–400°, reduced at 800–50°, and condensed at 250–320° in 60–70 or 80–90 min. with ~100% yield, contg. admixts.: Sb < 1×10^{-3}, Bi, Cr, Si < 10^{-3}, other metals <10^{-4}%. As_2O_3 redn. ran in 2 stages: (*1*) $As_2O_3 + 3C \rightarrow 2As + 3CO$; (*2*) $As_2O_3 + 3CO \rightarrow 2As + 3CO_2$. Hence both C and CO were reductors. Prepn. of pure As from As_2O_3 is more effective, its reaction being exothermic, and the yield 100%.
60: 5045d L. Ter-Oganian

The polymorphic modifications of arsenic trioxide. K. A. Becker, K. Plieth, and I. N. Stranski (Max-Planck-Ges., Berlin). *Prog. Inorg. Chem.* (F. Albert Cotton, editor. Interscience) 4, 1-72(1962).

Induced condensation of arsenic compounds II. K. A. Becker, W. Kollmitt, and I. N. Stranski (Max-Planck-Ges., Berlin-Dahlem). *Z. Physik. Chem.* (Frankfurt) 37(5/6), 314–27(1963); *cf.* Becker and Niesler, *CA* 58, 12017c. The velocity of the activated condensation is directly registered with a microbalance. The suggested course of reaction is: As_4O_6 mols. are dissocd. on the incandescent wire after a temp.-dependent accommodation. For the As_4O_6 and the As_2O_3 mols. a distribution of the translation and oscillation is established in the first moment in which the proportion of energy-rich mols. should be increased as compared with the equil. distribution by an energy-dependent factor. The activation energy of the condensation for the As_4O_6 mols. is by far greater than for the monomer. Thus, condensation is nearly completely effected by the excited As_4O_6 mols. 59 : 13763g Friedrich Epstein

Condensation experiments with As_4O_6. K. A. Becker, W. Schultze, and I. N. Stranski (Max-Planck-Ges., Berlin-Dahlem). *Z. Naturforsch.* 18a, 427(1963). When claudetite, $(As_2O_3)_n$, is sublimed in high vacuum at 260°, the only condensation product formed is arsenolite (As_4O_6) for receiver temps. of 100 to −196°. Higher temps. are evidently necessary for the formation of polymeric condensation products. D. H. De Voe

By product recovery of arsenic from wastes of metallurgical production. K. T. Akhmetov, N. N. Kubyshev, and K. S. Dashkov. *Tsvetn. Metal.* 36(2), 42–5(1963). The recovery of As and manuf. of a Cu–Cr–As wood preservative are discussed. 59 : 3602b E. M. Elkin

A metal-diaphragm apparatus for measuring vapor pressures. Vapor pressure of arsenic(III) oxide. F. D. Stevenson and C. E. Wicks (U.S. Bur. of Mines, Albany, Ore.). *U.S. Bur. Mines, Rept. Invest.* No. 6212, 19 pp.(1963). The sample is enclosed in a cylindrical chamber bounded by a valve on one end and a metal diaphragm on the other. As the system temp. increases, the sample vapor pressure distorts the diaphragm and closes an elec. indicator circuit. A manually controlled balance pressure applied to the other side of the diaphragm restores it to its null position. This balance pressure, after appropriate corrections, is then a measure of the vapor pressure. The vapor pressure of As_2O_3 was detd. to verify the reliability of the app. for such measurements. The data for liquid As_2O_3 (282–383°) are represented by the equation $\log P_{mm} = 6.875 - 2929/T$, from which the normal b.p. is calcd. to be 461°. The heat of vaporization calcd. from this equation is 13.40 ± 0.09 kcal./mole As_4O_6 and is const. over the interval studied. The m.p. of octahedral As_4O_6 was detd. to be 278° from the intersection of the solid and liquid vapor-pressure curves. A thermal-analysis app. is also described with which melting and transition temps. can be checked by a method independent of vapor-pressure data. The m.ps. of the monoclinic and octahedral forms are 314.4 ± 1.4° and 278 ± 3°, resp. 59 : 2179d C. W. Schuck

Formation of claudetite by forced condensation. K. A. Becker and R. A. Niesler (Max-Planck-Ges., Berlin-Dahlem, Ger.). *Z. Physik. Chem.* (Frankfurt) 36, 53–60(1963). The formation of the monoclinic As modification claudetite from the cubic arsenolite over the vapor phase generally occurs only in the presence of a catalyst, while the forced condensation of As vapors as a rule leads only to an amorphous phase. By suitable variation of condensation temp. and vapor pressure within the exptl. vessel claudetite could also be produced. Friedrich Epstein

Heat capacity of crystals of glass-forming substances at low temperature. V. A. Romanovskii (D. I. Mendeleev Chem.-Technol. Inst., Moscow). *Zh. Fiz. Khim.* 36, 2550–2(1962); *cf. CA* 56, 8082*d*. The effect was studied of the temp. on the heat capacity of crystals of readily vitrified substances by Tarasov's relation for chain type packing (*CA* 39, 5163⁴) in the interval of the derived temp. T/θ, from 0.05 to 0.25. The temp. ranges of agreement with theory were, for SiO_2, GeO_2, and B_2O_3, (74 to 297), (63 to 236), and (96 to 270°)K., resp. The packing d. of these crystals was 2.66 for SiO_2 and GeO_2 and 2.4 for B_2O_3. Similar results were obtained with As_4O_6 and As_2O_3 with a packing of 2.4 (*CA* 56, 8082*d*). Since the av. coordination no. of good glass-forming substances with a continuous structure of chem. bonds is not larger than 2.66 it was plausible to assume that the heat capacity-temp. relation of all these substances will be expressed by Tarasov's rule (*CA* 44, 4742*f*). CA

Behavior of arsenic acid at higher temperatures. A. Blazek, V. Ceslavska, and V. Frei (Metalurgicky Ustav CSAV, Prague). *Collection Czech. Chem. Commun.* 27, 1014–18(1962)(in German). Dehydration of arsenic acid and the decompn. of As_4O_6 were studied by thermogravimetric and by differential thermal analyses. The following hydrates are formed: $As_4O_6.4H_2O$, $As_4O_6.3H_2O$, and $As_4O_6.2H_2O$, which were detected previously by different methods. The hemihydrate $As_4O_6.0.5H_2O$ was formed. The pentahydrate $2As_4O_6.5H_2O$ was found instead of the pentahydrate $3As_4O_6.5H_2O$ described in the literature. E. Erdos

The vacuum condensing point (VCP) in sublimatography. I. Kiyoshi Yoshimura (Sophia Univ., Tokyo). *Bunseki Kagaku* 11, 397–400(1962). The VCP in sublimatography was studied to establish the sepn. of mixed systems by sublimation. When sublimed vapor condenses and crystallizes on the wall of a glass with a temp. gradient, a certain crit. point of condensation exists. The ratio (γ) of the pressure of the vapor phase to the satd. vapor pressure at the crit. point temp. is characteristic for each substance. The mean values of γ for $HgCl_2$, $HgBr_2$, HgI_2, SnI_4, AsO_3, and P_2O_5 are 1.50, 1.40, 1.72, 1.42, 1.79, and 1.99, resp. II. *Ibid.* 400–6. In order to examine the effect of vapor flow on the VCP in sublimatography, fundamental expts. were carried out by 2 methods (effusion and a direct method). For the relation between the vapor flow F (mole/sec.) in the glass tube with a temp. gradient and the VCP, an empirical formula $(\gamma P_s)^n = k'F$ was obtained, where γ is P_s/P_0 (P_s = pressure of vapor phase and P_0 = satd. vapor pressure at the temp. of the VCP), k' a const. related to the heating temp. t_h of the substance, and $n = 2$ or 1.4 when detd. by the effusion or by the direct method. VCP evidently depends upon t_h, and under fixed conditions, the position where the substance condenses in the tube, with a temp. gradient is detd. by t_h. The sepn. of any mixt. is conceivable from the t_h-VCP curve for each component in the mixt. Akimasa Masuda

Forced condensation of arsenic. K. A. Becker, G. Graf, and I. N. Stranski (Max-Planck-Ges., Berlin-Dahlem). *Z. Physik. Chem.* (Frankfurt) 30, 76–89(1961).—For the formation of a forced condensate, preliminary thermal or elec. activation of the vapor mols. to be condensed is necessary. The influence of the deactivating impacts of excited mols. on the condensation phenomenon in thermal activation was studied. Condensations caused by excitation by ion impact are described and an attempt is made to explain them quant. 56 : 5412d Friedrich Epstein

Evaporation processes of arsenolite and claudetite crystals. K. A. Becker, H. J. Forth, and I. N. Stranski (Tech. Univ., Berlin-Charlottenburg). *Z. Elektrochem.* 64, 373–80 (1960).—An elec. double balance is described that permits simultaneous measurement, during evapn., of the evapn. rate and of the impulse exerted on the support, and the recording of both quantities. With the Hertz-Knudsen equation, these 2 quantities permit calcn. of an effective (mean) mol. wt. of the evapg. particles. The balance is calibrated by measurements on Cd and Zn. Arsenolite (I) evaps. as As_4O_6, claudetite (II) depending on surface characteristics as mixts. of As_2O_3 and As_4O_6. The results are discussed in terms of the lattices of I and II, and suggestions for the mechanism of the evapn. are given. H. H. Jaffé

Specific heat and heat content of compounds of cadmium, mercury, arsenic antimony, and bismuth. A. N. Krestovnikov, M. S. Vendrikh, and E. I. Feigina. *Sbornik Nauch. Trudov Moskov. Inst. Tsvetn. Metal. i Zolota i Vsesoyuz. Nauch. Inzhener.-Tekh. Obshchestvo Tsvetnoi Met.* 1957, No. 28, 223–38.—A crit. evaluation of bibliographic data on the sp. heat and heat content of CdO, CdS, $CdCl_2$, HgO, HgS, Hg_2SO_4, HgCl, $HgCl_2$, As_2S_3, As_2O_3, As_2O_5, Sb_2O_3, Sb_2O_4, Sb_2O_5, Sb_2S_3, $SbCl_3$, Bi_2S_3, and Bi_2O_3 is given. 25 references. From *Referat. Zhur., Met.* 1958, Abstr. No. 14109.
54: 11682c K. L. C.

Polymorphism of arsenic trioxide. K. Plieth and I. N. Stranski (Fritz Haber Inst., Berlin-Dahlem). *Z. Physik* 156, 360–81(1959).—Evapn., condensation, melting, and dissolving of the 2 modifications (cubic and monoclinic) of As_2O_3 were studied. The influence of mol. structure on the kinetics of phase transitions is discussed. R. Nitsche

Heat capacity and enthalpy of arsenic. A. N. Krestovnikov. *Nauch. Trudy Moskov. Poligraf. Inst., Sbornik* 1957, Nos. 5–6, 225–7.—At low temps., C_p of As was measured by calorimetric adjustment of thermal resistance. From these data, H_t was calcd. T°K. and C_p are: 57.2, 2.400; 70.2, 2.580; 85.2, 3.536; 91.0, 3.703; 98.6, 3.880; 115.5, 4.481; 128.2, 4.620; 140.6, 4.800; 155.5, 4.990; 174.4, 5.137; 202.7, 5.418; 212.7, 5.526; 227.1, 5.692; 232.1, 5.743; 258.9, 5.767; 276.2, 5.734; 272.8, 5.754; 283.7, 5.818; 291.0, 5.900. T°K. and H_t are: 0, 0; 50, 44; 100, 209; 150, 430; 200, 690; 250, 970; 273, 1110, 300, 1160. For normal, increasing, and high temps., the equation $C_p = 8.570 - (939.9/(t + 370))$ was compared with calcn. by use of the formula, $C_p = 5.17 + (2.34 \times 10^{-3}T)$. Differences ranged from 1.16 to 0.84%. By crit. comparison of C_p of As, a straight-line formula, suitable up to 560°, is offered: $C_p = 5.9 + 0.00262t$. Consequently, $H_t = 5.9t + 0.00131t^2$, accurate for solid As up to its m.p., 817°; t°C. and H_t are: 0, 0; 100, 600; 200, 1230; 300, 1800; 400, 2370; 500, 3280; 600, 4010; 700, 4770; 800, 5660. 53: 19552g Y. Hinuldoom

Free-energy functions for gaseous monoxides. L. Brewer and M. S. Chandrasekharaiah (Univ. of California, Berkeley). *U.S. At. Energy Comm.* UCRL-8713, 17 pp. 1959).—Free-energy functions for 38 gaseous monoxides are tabulated for every 500° interval from room temp. up to 3000°K. Electronic contributions were estd. by means of a simple ionic model approximation. Rotational and vibrational contributions were calcd. from available data on fundamental vibrational frequencies and equil. internuclear sepns. or from estns. of these obtained from Badger's rule or by interpolation. All mol. consts. for the alkali metal oxides were estd. 53: 16626h Martin Allen

Abnormal behavior of the modifications of arsenous oxide. I. N. Stranski and U. Winkler. *Proc. Conf. Interfacial Phenomena and Nucleation, Boston, 1951* 2, 167–90(Pub. 1955); cf. *C.A.* 41, 7182i; 44, 2815a.—The 2 forms of As_2O_3 [arsenolite (I) and claudetite (II)] are discussed as examples that violate the rules (*a*) of impossibility of overstating a crystal beyond a transition point (e.g., m.p.), (*b*) Ostwald that the frequency of nucleation is greater for a modification stable at the higher temp., and (*c*) that the modification stable at higher temps. has the greater crystal symmetry. An explanation of this behavior supported by previously published material is given. It is based on the requirement that the transition I → II requires splitting off of each As_2O_3 unit in the crystal of I and that the forced condensation of II results if the mols. are activated.
53: 13721g S. J. O'Brien

The solution, solubility, and transitions of arsenolite and claudetite in water and aqueous solutions. I. N. Stranski, K. Plieth, and I. Zoll (Tech. Univ., Berlin). *Z. Elektrochem.* 62, 366–72(1958); cf. preceding abstr.—Heats of soln. and of transition are detd. from soly. measurements at various temps. Initial rates of soln. are large for arsenolite (I), larger yet for claudetite (II). Transition expts. in acidic media indicate that nucleation of I is faster than that of II. 52: 13373e H. H. Jaffé

The transformation of cubic arsenolite to its monoclinic modification, claudetite. I. N. Stranski, K. Plieth, and I. Zoll (Tech. Univ., Berlin). *Z. Elektrochem.* 62, 362–6 (1958).—The transition from arsenolite to claudetite occurs only in the presence of a certain amt. of H_2O. The apparent energy of activation is 14 kcal. The course of the reaction depends on whether the temp. is const. or variable. The processes are discussed in detail. H. H. Jaffé

Reaction of arsenic sesquioxide, water, and Thüringer glass at low temperatures. K. Plieth, I. N. Stranski, and I. Zoll (Max Planck Gesellschaft, Berlin-Dahlem). *Z. anorg. u. allgem. Chem.* 292, 343–6(1957).—As_2O_3–H_2O mixts. (1:7–1:10), heated above 104° in Thüringer glass or at higher temps. for longer times in Jena, Duran, or quartz glasses, give a white arsenosilicate deposit, (I), on the walls above the mixt. x-ray examn. shows that I formed up to 170° has a glassy structure but is cryst. above 170°. The ds. are 2.15 and 2.30 g./cc., resp. *In vacuo* I loses about 4% H_2O up to 600° and As only above 900°. The temp. dependence suggests that the primary step is the splitting of As_2O_3 in the vapor phase by H_2O. Entrance into the silicate lattice is favored by high alkali content of the glass. 52: 7922b Richard H. Jaquith

Evaporation of arsenolite and claudetite. I. Karutz and I. N. Stranski (Max Planck Gesellschaft, Berlin-Dahlem). *Z. anorg. u. allgem. Chem.* 292, 320–42(1957).—The vapor pressures of arsenolite (I) at 100–40° and 215–300° and of claudetite (II) at 215–300° are given by $\log p$(mm. Hg) = $-(5451.8/T) + 11.4679$ and $\log p$ (mm. Hg) = $-(5252.3/T) + 10.9053$, resp. The heats of vaporization are 24.156 and 24.931 kcal./mole, resp.; the heat of transition is 0.775 kcal./mole. The two forms of II show no difference. I, which is metastable above the transition temp. (30° ± 30°, obtained by extrapolation of the vapor-pressure curves), is readily superheated above the b.ps. of I (278°) or II (309°). The superheating is attributed to the high activation energy of converting the structural units of I to those found in II or in the melt. The viscosities of melts at 328–430° ($\log \eta$ increases linearly with $1/T$, the activation energy for liquid flow is 22.3 kcal./mole) and their x-ray patterns suggest that II and the melts are structurally similar. H_2O prevents superheating of I above its m.p. Above 180° I evaps. at max. rate, corresponding to the Hertz-Knudsen relation; the condensation coeff., i, is 1 and the activation energy of vaporization agrees with the heat of vaporization. Below 180° the evapn. rate is not max. and the condensation coeff. is given by: $\log i = (-6513.7/T) + 17.53$. The activation energy of vaporization is 29.8 kcal./mole. From 100° to 300° II evaps. very slowly; $\log i = -(12,127/T) + 22.66$. The activation energy of vaporization is 55.5 kcal./mole. H_2O vapor accelerates the evapn. The evapn. mechanism is discussed in terms of an evapn. model suggested earlier (*C.A.* 48, 11863d). 52: 7232i Richard H. Jaquith

Surface tension and heat of vaporization of mercury, antimony, bismuth, and arsenic. S. N. Zadumkin. *Zhur. Eksptl. i Teoret. Fiz.* 27, 261–2(1954).—The formula derived earlier (*C.A.* 50, 5355a) for calcg. surface tension, σ, from the molar heat of vaporization was applied to metals having a rhombohedral lattice, Hg, Sb, Bi, As. The deviation between the calcd. values of σ and the exptl. values never exceeded 10%. 50: 12764 J. Rovtar Leach

Electrochemical determination of the transition point between the cubic and monoclinic modifications of arsenic trioxide. Hans Joachim Kirschning and Karl Plieth (Max Planck Ges., Berlin). *Z. anorg. u. allgem. Chem.* 280, 316–32(1955); *cf. C.A.* 49, 13934*f*.—E.m.f. of the cell H_2|0.33 *M* HClO$_4$|0.23–0.27 *M* HClO$_4$ satd. with As_2O_3|As_2O_3, modification at 25, 30, 35, 40, and 45° was measured. The results agree well with the measurements of Schuhmann on arsenolite (*C.A.* 18, 2278). These values lead to the following thermodynamic values for the transformation of arsenolite to claudetite if ΔC_p is about the same for each modification: $\Delta G^{298} = -180$ cal., $\Delta S^{298} = 3.11$ cal./degree, and $\Delta H^{298} = 747$ cal. The transition temp. was estd. to be 240°K.
50: 2254*b* B. P. Block

Thermodynamic investigations of the system of the cubic and monoclinic As_2O_3 modifications. H. J. Kirschning, K. Plieth, and I. N. Stranski (Fritz-Haber-Inst., Berlin-Dahlem). *Z. Krist.* 105, 172–82(1954)(in German).—The monoclinic As_2O_3 modification claudetite is the stable modification from −33° upwards. The following data were found: temp. of transformation = 240 ± 30°K., heat of transformation = 670 ± 100 cal., entropy of transformation = 2.80 cal./degree, enthalpy of formation for arsenolite = −157,000 cal., for claudetite = −156,160 cal., free enthalpy of formation for arsenolite = −137,800 cal., for claudetite = −137,980 cal., entropy of formation for arsenolite = −64.44 cal./degree, for claudetite = −61.60 cal./degree, abs. entropy = S^{298} = +25.89 cal./degree (arsenolite) and +29.33 cal./degree (claudetite).
49: 13928*d* W. Nowacki

Transformations and structure of vitreous arsenious oxide. Karl Plieth. *Proc. Intern. Symposium Reactivity of Solids, Gothenburg* 1952, Pt. 2, 761–70(Pub. 1954)(in German).—Under certain conditions, roasting of As-bearing ores results in a colorless mass of glassy As_2O_3 (after resublimation) that has a conchoidal fracture and sp. gr. 3.70, slowly recrystallizes spontaneously, becomes opaque like porcelain, and forms cubic-octahedral crystallites of d. 3.87. This easy transformation seems to hint at (at room temp.) a closer relation between the glassy state and the regular arsenolite than in between the arsenious oxide glass and the monoclinic claudetite. In a vacuum vessel that contains the solid phase arsenolite, As_2O_3 is condensed from the vapor phase in the neighborhood of an incandescent coiled filament, though at this place there is a higher temp. than at the existing arsenolite phase. The explanation is a decomposition-recombination process in the vapor phase between the filament and the walls of the vessel. The condensate has, immediately after its formation, a glassy structure, and its gradual transformation into a cryst. form can be observed by means of x-rays or photomicrography. Mech. working of the freshly prepd. condensate in the air (scratching, rubbing, or pulverizing) favors the devitrification. Temps., up to 200°, favor the transition to the cryst. arsenolite state; still higher temps. yield a claudetite structure. These transformations are demonstrated with the aid of photomicrographs in the text (also from arsenic glass customarily prepd. by slow cooling of a melt) and with x-ray-diffraction curves. 42: 11366*d* Manfred Mannheimer

The dissociation of arsenic anhydride. Henri Guérin and Robert Boulitrop. *Compt. rend.* 236, 83–5(1953).—The equil. const. for $2As_2O_3$ (*c*) $\rightleftarrows As_4O_6$(*g*) + $2O_2$ was obtained by heating As_2O_3 in sealed, evacuated ampuls and measuring the vol. of O formed. The const. as a function of the abs. temp. is given by $RT \log K_p = -149{,}500$ cal. + 161.5 *T*. The calcd. dissocn. pressure is 10^{-7} atm. at 250° and 1 mm. at 300° in accord with the observation that As_2O_3 does not lose wt. when heated at 250° for 12 days, whereas formation of O is noted at 450° (but *cf.* Dupuis and Duval, *C.A.* 44, 10581*c*). 47: 6222*c* Edward J. King

The forced condensation of arsenic oxide. A theory for the rate of vaporization from crystals. Ivan N. Stranski and Günther Wolff. (Kaiser-Wilhelm-Inst. phys. Chem., Elektrochem., Berlin-Dahlem, Ger.). *Z. Naturforsch.* 4a, 21–7(1949); *cf. C.A.* 43, 5250*c*.—A theoretical discussion of the vaporization and condensation of As oxides.
44: 2215*a* H. Tarkow

The forced condensation of arsenic oxide. A theory for the rate of vaporization from crystals. I. N. Stranski and G. Wolff. *Z. Elektrochem.* 53, 1–4(1949).—A theoretical discussion of the vaporization and condensation of As oxides.
43: 5250*b* H. Tarkow

Heats of formation of oxides and of silicates. A. I. Avgustinik. *J. Applied Chem.* (U.S.S.R.) 20, 327–30 (1947)(in Russian).—Heats of formation ΔH of oxides plotted against the at. no. of the element show the periodicity common to many other properties. Elements of the 3rd and 5th group show characteristic peaks with lows for the neighboring 4th-group element; in the 1st subgroups, the values of the ΔH increase towards the 7th group; in the 2nd subgroups they decrease. Halogens and the metals of the 1st subgroup occupy the lowest points; the "amplitude," i.e. the spread between the peak and the lowest point, increases towards the 7th group. From the periodic chart of the known ΔH values, one can est. the unknown ΔH of As_2O_5, PdO, Ta_2O_5, SnO_2, Ga_2O_3, UO_3, and Pa_2O_5, to 270, 10, 400, 500, 110, 270, and 220 kcal./mole, resp. Survey of the heats of formation of silicates from SiO_2 and metal oxides in varying ratios shows decrease of the heat of combination with each successive mol. added, e.g.: $K_2O + SiO_2 = K_2O.SiO_2 + 63$ kcal.; $K_2O.SiO_2 + SiO_2 = K_2O.2SiO_2 + 13.8$; $K_2O.2SiO_2 + 2SiO_2 = K_2O.4SiO_2 + 4.6$, or: $SiO_2 + CaO = CaO.SiO_2 + 21.8$; $CaO.SiO_2 + CaO = 2CaO.SiO_2 + 8.18$; $2CaO.SiO_2 + CaO = 3CaO.SiO_2 - 0.52$; a similar decrease can be expected in each homologous series of silicates, also in titanates and in zirconates. 42: 1796*g* N. Thon

The polymorphism of arsenious oxide. James H. Schulman and Walter C. Schumb. *J. Am. Chem. Soc.* 65, 878–83(1943).—The monoclinic form of arsenious oxide is shown by soly. measurements to be thermodynamically stable with respect to the more common octahedral form at temps. as low as 2°. By calcns. based on the measured temp. dependence of the solubilities, it is shown that an enantiotropic relation exists between the two forms, the transition temp. being approx. −13°. The heat of soln. of both forms of the oxide in 1 *M* HCl and the latent heat of the transformation of octahedral As_2O_3 to the monoclinic form are calcd. from the above data. The latent heat of this transformation was likewise detd. calorimetrically by measurements of the heats of soln. of both forms in NaOH soln. The value so obtained is in good agreement with the calcd. value. The vapor pressures of the octahedral and monoclinic oxides were measured, and the data obtained by previous investigators are reviewed. The vapors of several substances were found ineffective for accelerating the transformation of octahedral to monoclinic As_2O_3 at 120°, whereas the effectiveness of water vapor at this temp. was confirmed. A qual. picture of the mechanism of the transition is presented. The prepn. of three new forms of arsenious oxide, whose existence was assumed by previous investigators on the basis of vapor-pressure measurements, was attempted without success. A. B. Garrett

Crystallization of arsenious oxide from the gas current according to the cocurrent principle. Determination of the proper construction of the arsenic-recovery apparatus. P. I. Deryagin. *Trudy Ural. Ind. Inst.* 1940, No. 14, 92–131; *Khim. Referat. Zhur.* 1940, No. 9, 74–5.—The crystn. of As_2O_3 is regarded as a recovery of mech. dust, without consideration of the growth of crystals in the gas. The process is carried out usually in chambers working under an erroneous principle of horizontal crystn., producing a fine, low-grade, cryst. product, with large losses into the atm. The crystn. process was examd. exptly. and mathematically by 3 methods: with a horizontal motion of the gas current, according to the countercurrent principle and according to the cocurrent principle. According to the cocurrent principle, with gradually increasing rate of cooling of the gas, the course of the process in the crystn. tower with a gradually decreasing thickness of walls from top to bottom and with a supplementary artificial cooling of the gas at the bottom of the tower, there are formed coarse, uniform and easily recovered crystals of high purity. There is an empirical relation between the rate of the growth of crystals and the concn. and rate of cooling of the gas. This relation is expressed by $y = a10^{q}$, which is sufficiently accurate for plant conditions (y is the no. of concn. centers, q the cooling rate in degrees per sec., and a a value which changes with the concn.). A method for calcg. the growth of crystals during uniform and during accelerated cooling of the gas is given and the construction of a tower for crystg. As_2O_3 according to the cocurrent principle is described. 37: 10173 H. R. Henn

High-vacuum sublimation as a method for detecting and concentrating rare elements. B. K. Veselovskii. *Zavodskaya Lab.* 10, 372–4(1941).—The app. used was essentially that of Klemm and Vogel and the vacuum was of the order of 10^{-3}–10^{-4} mm. Hg. Minerals subjected to sublimation were sphalerite and chalcopyrite. The results indicate that with sphalerite the Sb, Sn and Pb went over almost completely into the sublimate while Cd and Ag were divided about evenly between the sublimate and the residue. Spectral analysis showed no Ge in the mineral (less than 0.0001%) but the sublimate had about 0.001% Ge. The chalcopyrite had a complex compn. and was sublimated stepwise. The As was sublimated almost completely in the first two stages, Sb showed small amts. in the residue after two stages, and the sulfides of Sn, Ge and Pb were concd. chiefly in high-temp. (800–850°) sublimates. Ge was present in the sample in 0.001% and in the second sublimate in 0.01–0.1%. Spectral analysis showed no Ge in the residue after second sublimation (less than 0.0001%) but in the third sublimate it was present in up to 0.001%. Ga and In remained in the residue completely and were not present in the 800–850° sublimates.
35: 7293 B. Z. Kamich

Determination of heat consumption in the vaporization of metals or metal compounds. M. Richnow. *Metall u. Erz* 38, 32–5(1941).—A *calorimeter furnace* for detn. of the heat of vaporization of metals or metal compds. is described. This was detd. for the following substances to be as follows, expressed in cal. per g.: Cd 236.4, Zn 383.4, Hg 1917.4, As_2O_3 (stable and labile forms) 75.5, As_2S_3 83.7. Alloys in which the constituents form chem. compds. have higher vaporization heats than their components and these are of the same order as their heats of formation. 35: 5026 H. Stoertz

Crystal growth from the vapor phase. Johannes Ehlers. *Schr. mineral.-petrog. Inst. Univ. Kiel* No. 2, 24 pp.(1935); *Chem. Zentr.* 1937, I, 1639.—The growth of As_2O_3, $HgCl_2$, HgI_2 and $HgBr_2$ crystals from the vapor was studied in a newly constructed sublimation furnace. In all the expts. only the octahedron appeared as a growth form of As_2O_3. The following is assumed to explain this phenomenon: An adsorption-condensation layer forms on the growth surface, in which nuclei formation and deposition on the nuclei occur. The As_2O_3 lattice is a mol. lattice which is stable in the mol. As_2O_3 even in the gaseous state. During the building up of crystals the groups always arrange themselves on one another according to the (110) planes, so that this direction is given as the resultant of 2 (111) directions at angles to each other. Every 3 (110) directions coming together under 60° give an octahedral surface. This and the octahedral arrangement of the O atoms makes the exclusive appearance of the (111) arrangement as a growth form reasonable. With this manner of formation of the faces and with the (110) as the building direction parallel coalescence, fusiform twinning and skeletal formation can be explained. Expts. with $HgBr_2$ showed new, rhombic types of growth. In the case of the solid soln. $HgBr_2$.HgI_2 the phenomena typical of solid solns., as zones and sandglass structure, were shown. 32: 7323 W. A. Moore

Behavior of arsenious anhydride in hot gases during evaporation with other oxides. I. M. Dubrovin. *J. Applied Chem.* (U. S. S. R.) 9, 2145–51 (in German 2151–2)(1936).—The relative content of As^V in the reaction products at 400° and 250° is greater when As_2O_3 is suspended in heated gases, than when the same oxide is heated in a small boat at the same temp. Water vapor inhibits As salt formation at 400° and promotes it at 250°. SO_2 inhibits As salt formation in all cases. Six references. 31: 4221 A. A. Podgorny

Affinity of metals for sulfur. E. V. Britzke and A. F. Kapustinskii. *J. Phys. Chem.* (U. S. S. R.) 5, 85–90 (1934); cf. *C. A.* 25, 1430; 26, 2637, 2638, 2914, 3428.—The heats of formation of various sulfides from the metal and rhombic S were detd. as follows: FeS 18.0, SnS 18.5, Sb_2S_3 38.3, As_2S_3 (amorph.) 9.6, As_2S_3 (cryst.) 23.9, As_2S_5 (amorph.) 34.75, Cu_2S (cryst.) 20, As_2O_3.SO_3 23.03, As_2O_3.As_2O_5 −24.5. A table is given showing that as the radii of the metal ions increase the electrolytic dissocn. consts. of sulfides decrease while the thermal dissocn. consts. increase. Determination of the heat of formation of disulfides and trisulfides of arsenic. E. V. Britzke, A. F. Kapustinskii and L. G. Chentzova. *Ibid.* 91–6 (1934); cf. *C. A.* 27, 4008.—On the basis of data obtained from the combustion of As_2S_3 and As_2S_5 with the formation of SO_3 and a mixt. of As_2O_3, As_2O_3.As_2O_5 and As_2O_3.SO_3, the heats of formation of solid As_2S_3 and As_2S_5 from solid As and rhombic S are calcd. as 28.9 and 34.7 Cal., resp. Determination of the heat of formation of double compounds of pentoxide and trioxide of arsenic, and the heat of formation of sulfate of arsenic. *Ibid.* 97–102(1934).—The heats of formation of As_2O_3.SO_3 from solid As_2O_3 and gaseous SO_3 and of solid As_2O_3.As_2O_5 from solid As_2O_3 and solid As_2O_5 are 23.03 and −24.5 Cal., resp. The heats of soln. of As_2O_3 and As_2O_5 in NaOH (0.83 *N*) are +9.61 and +63.23 Cal., resp. F. H. R.

The complexity of arsenic trioxide. A. Smits and E. Beljaars. *Z. physik. Chem.* A167, 273–94(1933).—The *P-T* diagram of As_2O_3 was accurately detd. between 240° and 390°. Below 240° the vapor pressure was too low to measure accurately. From soly. detns. in Et benzoate solns., the octahedral modification of As_2O_3 is stable below 221° and the monoclinic modification is stable above 221°. The stable triple point, $S_1 + L + G$, was found at 312.3° and 66.1 mm. Hg the metastable triple point, $S_1 + L + G$, at 272.1° and 28.1 mm. Hg. A change of the S_1 modification to a hitherto unknown S_2 modification was observed in the metastable region at 258.4°. This metastable S_2 modification reached its triple point, $S_2 + L + G$, at 289.6° and 40.7 mm. Hg.
28: 2252 Don Brouse

Complexity of arsenic trioxide. II. A. Smits and E. Beljaars. *Proc. Acad. Sci. Amsterdam* 34, 1318–23(1931); cf. *C. A.* 26, 3711.—The following data were detd.: mol. heat of sublimation (g.-cal.), α-As_2O_3 23,676, β-As_2O_3 29,833, γ-As_2O_3 21,130; mol. heat of vaporization (g.-cal.), α-As_2O_3 14,734; mol. heat of melting (g.-cal.), α-As_2O_3 5912, β-As_2O_3 15,099, γ-As_2O_3 6396. Equil. diagrams are given and explained in terms of Smits' theory of allotropy. 26: 4993 B. C. A.

Contributions to the data on theoretical metallurgy. I. The entropies of inorganic substances. K. K. Kelley. *Bur. Mines, Bull.* 350, 63 pp.(1932).—Entropies at 298.1°K. are given for those elements and common compds. for whose calcn. the necessary data are available, *i. e.*, Al, Al_2O_3, Al_2SiO_5 (disthene, sillimanite and andalusite), Sb, Sb_2O_3, Sb_2O_4, Sb_2O_5, A, As, As_2O_3, As_2O_5, Ba, $Ba(NO_3)_2$, Be, Bi, Bi_2O_3, Br_2, Cd, CdO, CdS, Ca, CaO, CaS, CaF_2, $CaCO_3$ (aragonite and calcite), CaH_2, $Ca(OH)_2$, $CaSiO_3$, C (diamond and β-graphite), CO, CO_2, CH_4, Ce, CeO_2, Cl_2, Cr, Co, Cu, Cu_2O, CuO, Cu_2S, CuS, CuI, Ga, Ge, Au, He, H, H_2O, HBr, HCl, HI, HF, H_2S, In, I_2, Ir, Fe, FeO, Fe_2O_3, Fe_3O_4, FeS, FeS_2, La, Pb, PbO, PbO_2, Pb_3O_4, PbS, $PbBr_2$, $PbCl_2$, PbI_2, Li, LiH, Mg, MgO, Mn, MnO, MnO_2, Mn_2O_3, MnS, Hg, HgO (red and yellow), HgCl, Hg_2SO_4, HgS, Mo, Ne, Ni, NI, N_2, N_2O, NO, NH_3, NH_4Cl, O_2, O_3, Pd, Pt, K, KBr, KCl, $KClO_4$, KI, Pr, Rh, Rb, Ru, Sc_2O_3, Si, SiO_2 (quartz, christobalite and glass), SiC, Ag, Ag_2O, AgBr, AgCl, AgI, Na, NaCl, S (rhombic and monoclinic), SO_2, Ta, Tl, TlBr, TlCl, TlI, Th, ThO_2, Sn (white and gray), SnO, SnO_2, Ti, W, WO_3, U, U_3O_8, V, Xe, Zn, ZnO, ZnS, Zr and electron gas. Methods of calcn. are discussed. A bibliography of about 400 references is given. 26: 4234 9 Alden H. Emery

The complexity of arsenic trioxide. A. Smits and R. Beljaars. *Proc. Acad. Sci. Amsterdam* 34, 1141–55(1931).—As_2O_3 purified by repeated sublimation at 320° under reduced pressure, after heating for 6–8 hrs. at 200° gave the vapor pressure following in parentheses. Each sample was maintained at the temp. indicated for 20 min. 239.8° (4.5 mm.), 253.2° (9.3), 264.8° (18.3), 270.0° (23.4) and for the liquid the following: 273.4° (24.9), 293.7° (43.0), 307.4° (59.9), 318.9° (77.1), 333.2° (102.5), 363.1° (163.6). The vapor pressures of the supercooled liquids were resp., 265.9° (22.9), 243.5° (12.7). If the heating is not continued too long the metastable sublimation curve is followed; it passes through a max. and decreases to cut the liquid-vapor line. On this sublimation curve are the following values: 278.3° (37.5), 293.4° (68.0), 309.0° (111.2), 318.9° (122.9) (max.), 326.7° (94.1). The octahedral form (here designated β) when long heated above 258° and then slowly heated gave a m. p. 17° higher because of the appearance of another form (γ). The monoclinic (α) form vapor-pressure curve passed through the points: 243.1° (4.9), 253.4° (7.6), 263.8° (11.7), 274.2° (17.2), 279.3 (21.4), 284.6 (24.8), 289.8° (31.1), 295.1° (31.1), 295.1° (37.2). After partial fractionation the remainder gave much lower values on the ascending curve, but on descending followed the α-curve as follows: 263.8° (2.3), 274.2° (9.61), 279.3° (15.9), 284.6° (22.4), 289.8° (29.5), 295.1° (37.2). The monoclinic behaves as a mixed cryst. phase in which equil. is disturbed by partial distn. accounting for the abnormally low vapor-pressure values of the remainder. The same material that gave the abnormally low vapor pressure on the heating curve was partially sublimed in a closed vessel and the vapor pressure of the freshly sublimed portion yielded the following abnormally high values: 243.1° (39.4), 263.8° (57.0), 274.2° (65.7), 279.3° (69.2), 284.6° (74.2), 289.8° (77.7), 295.1° (80.1), 310.0° (77.7), 315.7° (75.9). This is the sublimation curve of the γ form. Stable triple points detd. were: α-β-vapor, about 200° (0.26), α-liquid-vapor at 312.3° (66.1) and the metastable points; β-liquid-vapor at 272.1 (26.1), β-γ-vapor at 253.4 (13.9) and γ-liquid-vapor at 289.6° (40.7). 26: 3911 9 A. Lloyd Taylor

The reaction $5As_2O_3 \longrightarrow 3As_2O_5 + 4As$ as a pyrochemical and photochemical process. Georg Günther Reissaus. *Z. angew. Chem.* 44, 959–62(1931).—Instead of the accepted reaction $As_2O_3 + O_2 \longrightarrow As_2O_5$ showing the course of the change, expts. and metallurgical practice indicate that oxidation takes place thus: (*a*) $5As_2O_3 \longrightarrow 3As_2O_5 + 4As$, (*b*) $10R_3AsO_3 \longrightarrow 6R_3AsO_4 + 6R_2O + 4As$, (*c*) $6R_3AsO_3 + 2As_2O_3 \longrightarrow 6R_3AsO_4 + 4As$ (all 3 reactions without access to O_2). (*d*) $6R_3AsO_3 + 2As_2O_3 + 5O_2 \longrightarrow 6R_3AsO_4 + 2As_2O_5$ and (*e*) $As_2O_3 + O_2 \longrightarrow As_2O_5$. Proof is adduced from results of roasting speiss, heating arsenous compds. in absence and in presence of O_2, and the formation of metallic arsenites and arsenates. Pb arsenite drying in a dark air bath remained white, but exposed to light it turned brown. Mixed with gelatin, painted on paper and dried in the dark it yielded a photographic paper which developed warm sepia tones when exposed under a negative. Light sensitivity is not possessed by all $Pb_3(AsO_3)_2$; a mixt. of dry As_2O_3 and PbO, and the salt formed from $3Pb(OH)_2$ and As_2O_3, were specially active to light. No other metallic arsenites proved to be light-sensitive. It seems that a metal capable of forming a dioxide must be used. 26: 1205 W. C. Edaugu

The heat capacities of arsenic, arsenic trioxide and arsenic pentoxide at low temperatures. C. Travis Anderson. *J. Am. Chem. Soc.* 52, 2296–300(1930).—The heat capacities of As, As_2O_3 and As_2O_5 were detd. from about 57° to 300°K. The corresponding entropies, the heat of formation of As_2O_3 and the free energy of formation of As_2O_5 were calcd. 24: 3946 3 C. L. Read

Vapor pressure of arsenic trioxide. E. R. Rushton and Farrington Daniels. *J. Am. Chem. Soc.* 45, 334–9 (1923).—Although octahedral As_2O_3 (m. 275°) is metastable above 100°, the rate of change to the stable monoclinic form (m. 315°) is so slow as to permit measurements of the vapor pressure of the former up to 250° or higher, depending on the rate of heating. The equation for the vapor-pressure curves are: octahedral form $\log P = -(6670/T) + 13.728$; monoclinic form given provisionally as $\log P = -(6100/T) + 12.26$; and liquid, $\log P = -2732/T + 6.513$. From the Clausius-Clapeyron equation the heats of vaporization are calcd. as: liquid, 31.5 cals.; octahedral, 77.1 cals.; monoclinic 71 cals. 20: 1157 James M. Bell

The free energy and heat content of arsenic trioxide and the reduction potential of arsenic. Reinhardt Schuhmann. *J. Am. Chem. Soc.* 46, 1444–9(1924).—The e. m. f. of the cell $As(s) + As_2O_3(s), HClO_4(0.22\text{–}0.94\,M), H_2$ (1 atm.) was measured at 25° and 45°, and the resp. values were −0.2340 and −0.2250 v. The free energy at 25° of As_2O_3 (octahedral) referred to cryst. metallic As (sublimed) = −137,300 cal. Its heat content, ΔH as derived from the cell measurements at the 2 temps. = −153,800 cal. The soly. of As_2O_3 in $HClO_4$ soln. decreases with increased concn. of $HClO_4$. Presumably all the arsenic in such solutions is in the form $HAsO_2$. On this assumption, the reduction potential of As ($As + 2H_2O + 3\ominus = HAsO_2 + 3H^+$) is 0.2375 v. F. R. B.

Vapor pressure of arsenious oxide. P. Sheller. *J. Soc. Chem. Ind.* 42, 466–8T (1923); cf. Schwers, *C. A.* 14, 1212.—The vapor pressures detd. by the air current method with As_2O_3 in H_2SO_4 were not reliable because of decompn. of H_2SO_4. The vapor pressures of pure As_2O_3 are as follows: 60.8°, 2.4×10^{-4}; 83°, 2.5×10^{-4}; 103°, 4.6×10^{-4}; 119°, 1.9×10^{-3}; 121°, 2.2×10^{-4}; 142°, 1.4×10^{-3}; 150°, 2.6×10^{-3}. 18: 1093 P. D. V. Manning

Determination of the vapor pressure of metallic arsenic. Shinkichi Horiba. *Proc. Acad. Sci. Amsterdam* 25, 387–94(1923).—From the viewpoint of the theory of allotropy As is an interesting study. The results are given only for the gray modification. The method is that used by Smits and Bokhorst (*C. A.* 10, 2857) in studying P. The results agree closely with the equation $T \log p = -7257 + 8.279\,T$ (solid); $T \log p = -2450 + 3.80\,T$ (liquid), p being in atm. The triple point is between S17° and S18°, the corresponding pressure being 36.8 atm. 17: 2210 E. D. Williamson

Vapor pressure of arsenious oxide in sulfuric acid solutions. F. Schwers. *J. Soc. Chem. Ind.* 39, 33–5T(1920).—The vapor pressure of As_2O_3 in H_2SO_4 soln. was detd. by slowly bubbling metered air, dried and freed of CO_2 through 6 bubblers containing the solution and immersed in a water thermostat maintained at 60°. The exit air was carefully freed of spray and passed into 5 absorbers half filled with 10% NaOH soln. The As_2O_3 caught in the absorbers was detd. by Thorpe's electrolytic method. When pure H_2SO_4 (d. 1.84) had added to it 0.015% As_2O_3, the vapor pressure of the As_2O_3 was found to be slightly above 0.00001 mm. of Hg (0.000192 g. per cu. m. at 60°). When acid used in a contact plant for purifying burner gas, and containing 0.001% As_2O_3, was used the vapor pressure of the As_2O_3 was found to be 0.0000007 mm. of Hg (0.000013 g. per cu. m. at 60°). The agreement between the concn. of the As_2O_3 solns. and the amt. carried over is very striking but probably partly due to chance, since the probable error in analysis is of the order of 10%. It is shown that though the abs. magnitude of these pressures is small the amt. of As carried into the contact mass by the dried gases may in practice be enough to poison the platinum. 14: 1242 F. C. Z.

Researches at high temperatures. XII. The measurement of vapor pressure at very high pressures and the solubility of carbon in metals. OTTO RUFF AND EBERHARD BERGDAHL. Berlin. *Z. anorg. allgem. Chem.* 106, 76–94(1919); cf. preceding abstr.—Vapor-pressure measurements were made by suspending the substance from a spiral balance by a silica or W suspension in an elec. furnace, in an inert atm. at a definite pressure, and noting the change in wt. with increasing temp. At the b. p. under the existing pressure the rate of evapn. changes, and by altering the pressure the *P-T* curve could be mapped out. The detailed results are: Cd 530°, 16 mm.; 560°, 32; 583°, 47; 628°, 71; 707°, 292; 721°, 415; 758°, 576; 782°, 731; 785°, 760 mm. Zn: 653°, 15 mm.; 740°, 64; 830°, 239; 870°, 317; 876°, 379; 885°, 468; 925°, 733; 930°, 760 mm. As: 439°, 38 mm.; 483°, 75; 510°, 170; 520°, 205; 550°, 302; 563°, 734; 568°, 760 mm. Sb: 1075°, 54 mm.; 1135°, 107; 1175°, 206; 1225°, 302; 1265°, 398; 1325°, 745; 1330°, 760 mm. Bi: 1210°, 63 mm.; 1290°, 126; 1385°, 300; 1410°, 406; 1490°, 760 mm. Pb: 1275°, 73 mm.; 1365°, 166; 1415°, 289; 1447°, 370; 1470°, 407; 1535°, 760 mm. Sn: 2003°, 126 mm.; 2045°, 178; 2160°, 372; 2190°, 485; 2193°, 500; 2270°, 760 mm. Cu: 2105°, 124 mm.; 2175°, 209; 2215°, 300; 2245°, 404; 2305°, 760 mm. Ag: 1660°, 102 mm.; 1680°, 116; 1738°, 200; 1810°, 300; 1940°, 744; 1950°, 760 mm. Au: 2315°, 130 mm.; 2450°, 296; 2480°, 332; 2500°, 400; 2610° 760 mm. The *P-T* curve for Hg was also detd. to test the method; results for it and for the other metals agree in general with previous observers, with the exception of Sb, Bi and Pb, which are not in accord with the results of Greenwood, and of As, which differ from those of Preuner and Brockmöller, in the latter case probably due to a lack of mol. equil. by the dynamic method. C crucibles were used in most cases; on evapn. flaky graphite was left behind, presumably having been dissolved by the metal. The following soly. of C in metal were on this assumption: Sb, 1327°, 0.094%; Bi, 1490°, 0.023%; Pb, 1535°, 0.94%; Cu, 2300°, 0.033%; Ag, 1940°, 0.022%; the soly. in Hg, Cd, Zn, As, Sn and Au was too small to be detd.

13: 3054 g

GEORGE W. MOREY

Thermodynamics: Arsenic Sulphides

84: 141568n High-temperature heat capacity of chalcogenide compounds in vitreous and crystalline states. Zigel, V. V.; Orlova, G. M.; D'yakova, G. N. (Leningr. Gos. Univ. im. Zhdanova, Leningrad, USSR). *Fiz. Khim. Stekla* 1975, 1(6), 563–61 (Russ). Temp. dependence of heat capacities C_p of cryst. and vitreous As_2Se_3, As_2Se_5, and $TlAsX_2$ (X = S, Se, or Te) was detd. at 300–600°K by an adiabatic calorimeter at a continuous heating of the samples at 0.03°/min. The systematic exptl. error was <±2%. The results show phase transitions. The excitation of sym. vibrations of all structural units of the chalcogenides and the approach of the sym. vibration energies to the deformational-vibration energies is reflected by a jump of the C_p values and by an inflection on the curve of temp. dependence of their viscous flow. The C_p of molten chalcogenides changed insignificantly with temp. The $TlAsTe_2$ glass crystd. at the exptl. conditions and its heat of melting was equal to its heat of crystn. (1.84 kcal/mole).

84: 50582p Vapor pressure and thermodynamic functions of arsenic sulfide (As_4S_4). Pashinkin, A. S.; Malkova, A. S. (Mosk. Inst. Elektron. Tekh., Moscow, USSR). *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1975, 11(11), 2066–7 (Russ). The vapor pressure of the mineral *realgar* [12044-30-3] (As_4S_4) was measured previously by Munir et al (1971) and by Gospodinov and Pashinkin (1973). In the present work the results of the two works were compared, and data are also presented regarding the thermodn. functions of the solid and the gaseous As_4S_4 [12279-90-2]. The data show that equil. vapor over liq. realgar consists of tetrameric mols. The existence of the As_4S_4 mol. is confirmed also mass-spectrometrically. Thermodn. functions of the gaseous As_4S_4 are calcd. and presented in tabular form. The heat capacity of solid As_4S_4 was detd. as 44.96 cal/deg·mole and the temp. dependence of the solid As_4S_4 also was studied.

84: 33289p Preparation of arsenic sulfide by a high-temperature fractional distillation method. Kuadzhe, B. M.; Kudryavtsev, A. A. (USSR). *Khim. Prom-st. (Moscow)* 1975, (7), 534–7 (Russ). Three methods for obtaining As_2S_3 for use in manufg. O-free glasses were investigated: leaching from ores, synthesis from the elements, and 2-stage distn. Batch distn. in a vacuum and at high temps. gave As_2S_3 that was most suitable.
Z. Sterbacek

72: 166522t Light enhanced vaporization of amorphous arsenic(III) sulfide. Jansi, M.; Rudman, P. S. (Dep. Phys., Technion-Israel Inst. Technol., Haifa, Israel). *Amorphous Liq. Semicond., Proc. Int. Conf., 5th* 1973 (Pub. 1974), 1, 425–30 (Eng). Edited by Stuke, J.; Brenig, Wilhelm. Taylor and Francis: London, Engl. Low intensity light irradn. was found to enhance the vaporization rate of thin films of amorphous As S. The rate of vaporization was measured as a function of light intensity and wavelength, temp., and O concn. in the ambient gas. A representative result is a vaporization rate of 1 Å/sec (light intensity 10^{-4} W/cm², wavelength = 0.4 μ, temp. = 150°, air ambient gas). The enhanced vaporization rate is not due to heating by the irradn. The effect is explained as a combination of photodecompn. and oxidn. reactions, and the vaporization of volatile reaction products.

82: 116451v Saturated vapor pressure of solid arsenous sulfide. Gospodinov, G. G.; Pashinkin, A. S. (Mosk. Gos. Univ. im. Lomonosova, Moscow, USSR). *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1974, 10(11), 2073–5 (Russ). The behavior of As_2S_3 during sublimation was investigated; the partial pressure of the satd. vapor below the m.p. was also measured. Knudsen and Langmuir methods were employed for the measurements. The As_2S_3 was prepd. by synthesizing stoichiometric amts. of the individual elements in evacuated quartz ampoule. In order to prep. the sample in a crystal state, the alloy was annealed for a prolonged time (2500 hr) at 250–200°C. The immediate purpose of the present work was to det. the pressure of the satd. vapor of solid As_2S_3. The pressure was detd. by Knudsen's method at 476–536°K, and at 470–544°K by Langmuir's method. Generally, the data coincided quite well with the reported literature values.
S. A. Mersol

82: 47910q Composition of arsenic(III) sulfide vapor. Pashinkin, A. S.; Molodyk, A. D.; Belousov, V. L.; Strel'chenko, S. S.; Fedorov, V. A. (USSR). *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1974, 10(9), 1600–2 (Russ). The compn. of the As_2S_3 [1303-33-9] vapor was detd. by mass spectrometry under conditions close to equil. Natural cryst. As_2S was employed as the sample. The sublimation process is basically detd. by the equation $As_2S_{3(s)} = 2/nAs_n(g) + 1/2S_2(g)$. The heats of reaction are presented, as well as the dissocn. energy of AsS(g) [12044-79-0] and the heat of sublimation of As_2S_3.
S. A. Mersol

71: 156363d Condensation of metal sulfides in a medium vacuum. Isakova, R. A.; Spivak, M. M.; Chelokhsaev, L. S. (USSR). *Zh. Prikl. Khim. (Leningrad)* 1974, 47(5), 959–63 (Russ). The condensation of some metal sulfides was studied at residual pressure 0.1 torr and evapn. rate 5×10^{-4} g/cm² sec under these conditions the initial condensation temps. were: ZnS >900°, CdS 785°, Bi_2S_3 500°, PbS 450°, In_2S_3 410°, Tl_2S 370°, Sb_2S_3 340°, and HgS 200°. The form and structure of the condensates depended on the condenser temp. and material. As_2S_3, Tl_2S, and PbS formed a liq. layer on the condenser surface far below their m.p. The condensates of In_2S_3, Ni_2S_3, and CdS contained their dissocn. products. This method was used for sepn. of the mixt. ZnS, PbS, Sb_2S_3 and As_2S_3 as well as Sb_2S_3 and HgS in a tube condenser with temp. regulation at residual pressure 0.1 torr. The sepd. sulfides contained ≤1–2% of other sulfides.
M. Vajart

30: 125452g Measurements of thermal conductivities and heat capacities for arsenic(III) sulfide and arsenic(III) selenide glasses. Kuriyama, Masaaki (Natl. Inst. Res. Inorg. Mater., Japan). *Yogyo Kyokai Shi* 1973, 82(3), 156–9 (Japan). Temp. dependences of the thermal cond. and heat capacity for As_2S_3 and As_2Se_3 glasses were measured by a continuous heating method in the temp. range from room temp. to the transition temp. range. The thermal cond. and heat capacity were measured easily and in a short time by this method. The thermal cond. of these glasses increased slowly with rising temp.; above the transition range, the cond. slightly decreased with increase of temp. Heat capacities of these glasses increased with rising temp. and in the transition range the temp. dependence showed a sudden change and had a max. Temp. dependences of sp. heats were detd. from the obsd. heat capacities and sp. gravities. The contribution of radiation heat transfer to the total heat transfer was estd. It is reasonable to consider the heat to be transfered only by conduction, since the contribution of radiation was negligibly small in this work.

82: 33391b Decomposition of arsenic trisulfide during vacuum sublimation. Govlovikov, A. A.; Nenashev, B. G.; Andreev, A. P. (Inst. Geol. Geofiz., Novosibirsk, USSR). *Dokl. Akad. Nauk SSSR* 1973, 212(5), 1196–8 [Mineral] (Russ). From an x-ray diffraction study, 3 temp.-dependent zones are obsd. during the vaccum sublimation of As_2S_3. A homogeneous orange-red glass (As_2S_3) is x-ray amorphous and obsd. at 90–100° condensing at ~80°. Finely cryst. β-As_2S_3 appears at 75–150°, and yellow cryst. S forms at 150°. Similar results were obtained with natural auripigment.
K. Volka

79: 24106w Vapor pressure study of arsenic trisulfide. Faure, F. M.; Mitchell, M. J.; Bartlett, R. W. (Dep. Appl. Earth Sci., Stanford Univ., Stanford, Calif.). *High Temp. Sci.* 1973, 5(2), 129–37 (Eng). The vaporization of As_2S_3 was studied by the mass spectrometric Knudsen effusion and by the thermogravimetric Knudsen effusion methods. The vaporization was congruent, primarily according to the reaction: $As_2S_3(s) = 2AsS(g) + 1/2S_2(g)$. Mass species heavier than AsS were minor. A 2nd law fit of the thermogravimetric Knudsen effusion data gave an enthalpy $\Delta H^\circ_{298} = 101$ kcal mole^{-1} and an entropy $\Delta S^\circ_{298} = 132$ gibbs mole^{-1}, but large uncertainties are attached to these values because of possible errors in temp. measurements. The 3rd law std. enthalpy of vaporization was $\Delta H^\circ_{298} = 86.6 \pm 2.2$ kcal mole^{-1} and the std. entropy of vaporation calcd. from the std. entropies of the species was $\Delta S^\circ_{298} = 106 \pm 1.6$ gibbs mole^{-1}. The enthalpy of formation and dissocn. energy of AsS(g) were estd.

79:101116n Vapor pressure of arsenic trisulfide in the arsenic trisulfide-sodium metathioarsenite-sodium orthothioarsenite system and over sodium orthothioarsenite. Polukarov, A. N.; Zhambekov, M. I.; Makhmetov, M. Zh.; Isabaev, S. M. (USSR). *Tr. Khim.-Met. Inst., Akad. Nauk Kaz. SSR* 1972, 19, 23–7 (Russ). By dew point measurements, the vapor pressure of As_2S_3 in the Na_3AsS_3–Na_3AsS_4 system and over Na_3AsS_4 was detd. at 370–450 and 780–940°. The vapor tension in Na_3AsS_3–Na_3AsS_4 system is lower than over pure As_2S_3 as a result of soln. formation. Equations of the plot of the log of As_2S_3 vapor pressure on $1/T$ are given. The m.p. of Na_3AsS_3 was 471°. The temp. of Na_3AsS_4 decompn. was 947° at 760 torr and the calcd. values for the heat and entropy of dissocn. in the As_2S_3–$NaAsS_2$–Na_3AsS_4 system were $\Delta H_{298}°$ = 22,528 cal/mole, $\Delta H_{T_m}°$ = 11,971 cal/mole, $\Delta S_{298}°$ = 24.7, and $\Delta S_{T_m}°$ = 10.5 entropy units. The heat and entropy of Na_3AsS_4 decompn. are $\Delta H_{298}°$ = 41,916 cal/mole and $\Delta S_{298}°$ = 34.4 entropy units, resp.

V. Pekarek

79:129054k Thermodynamics of vaporization of sulfides of antimony and arsenic. Faure, Francois Michel (Stanford Univ., Stanford, Calif.). 1972, 157 pp. (Eng). Avail. Univ. Microfilms, Ann Arbor, Mich., Order No. 73-4489. From *Diss. Abstr. Int. B* 1973, 33(8), 3576–7.

72:83668t Saturated vapor pressure of solid arsenic sulfide. Gospodinov, G. G.; Pashinkin, A. S. (Mosk. Gos. Univ. im. Lomonosova, Moscow, USSR). *Izv. Akad. Nauk SSSR, Neorg. Mater.* 1973, 9(1), 15–17 (Russ). The satd. vapor pressure of solid AsS was measured at 432–548°K by Knudsen's method. The heat of sublimation of As_4S_4 at 490°K is 28.5 kcal/mole. The heat of fusion of AsS is 2.8 kcal/mole. The comparison of the vapor pressure values as measured by Knudsen's and Langmuir's methods shows that in the 432–548°K temp. range, the vaporization coeff. varies within 0.09–0.01. S. A. Mersol

76:16801m Thermal decomposition of arsenopyrite in vacuum. Zviadadze, G. N.; Tabatadze, E. S. (USSR). *Vak. Poverkn. Tverd. Met.* 1971, 178–81 (Russ). From *Ref. Zh., Met.* 1971, Abstr. No. 6G330. Kinetics of FeAsS decompn. in vacuum was investigated. The possible purification of As by removal of S by using Cu_2As is proven.

75:144104h Mass-spectrometric and vapor pressure studies on the sublimation of realgar (As_4S_4). Munir, Zuhair A.; Street, G. Bryan; Winters, Harold F. (Sch. Eng., San Jose State Coll., San Jose, Calif.). *J. Chem. Phys.* 1971, 55(9), 4520–7 (Eng). The nature of the sublimation process for the mol. solid realgar (As_4S_4) was investigated by using mass spectrometric and vapor-pressure techniques. Vapor originating from the congruent sublimation of this compd. is composed predominantly of As_4S_4(g) mols., with smaller concns. of other species. Of these latter species, those of As_2S_2, As_4, and As_2 are believed to originate from partial decompn. of solid As_4S_4. The amt. of these decompn. products relative to As_4S_4(g) in the vapor phase decreases with increasing temp. The mass spectra of the vapors resulting from the sublimation of synthetic and natural samples of realgar were essentially the same. The expression for the equil. sublimation of realgar at 452–534°K is $\log P(\text{atm}) = (8.021 \pm 0.200) - (9.619 \pm 0.010) 10^3/T$. On the assumption that realgar sublimes primarily to As_4S_4(g) mols., the 2nd law heat and entropy for sublimation at 493°K were calcd. to be 28.3 ± 0.5 kcal/mole and 36.7 ± 0.9 entropy units, resp. From free surface sublimation studies the sublimation coeff. at 455°K was 0.47.

57955z Low-temperature specific heat of vitreous arsenic trisulfide. Tarasov, V. V.; Zhdanov, V. M. (Mosk. Khim.-Tekhnol. Inst. im. Mendeleeva, Moscow, USSR). *Zh. Fiz. Khim.* 1970, 44(9), 2384–7 (Russ). The heat capacity was detd. at 53–305°K in a vacuum adiabatic calorimeter. The exptl. values of C_p were tabulated and used, along with the elastic properties for As_2S_3 (A. Chernov, et al., 1968), to calc. C_v. The exptl. values of C_v are in agreement with those calcd. by using the one-parameter, chain function for the sp. heat capacity (Tarasov, et al., 1963). The quasi-dynamic vibration dynamics for the vibrations and the closeness of the characteristic temps. for cryst. and vitreous As_2S_3 lead to the conclusion that the system of directed covalent bonds is retained in the cryst. → glass transition in the form of a polymeric network. GLJR

73 39424y Heat capacities of glassy and liquid As_2S_3 and As_2Se_3. Schnaus, U. E.; Moynihan, C. T.; Gammon, R. W.; Macedo, P. B. (Vitreous State Lab., Catholic Univ. of America, Washington, D.C.). *U.S. Clearinghouse Fed. Sci. Tech. Inform., AD* 1969, No. 689542, 18 pp. (Eng). Avail. CFSTI. From *U.S. Govt. Res. Develop. Rep.* 1970, 70(4), 61. Heat capacities of glassy and liq. As_2S_3 and As_2Se_3 have been detd. over the resp. temp. intervals 180–650°K and 180–620°K. The heat capacity data indicate an effective Debye temp. difference of ~100°K between the sulfide and selenide glasses, which is approx. the difference expected on the basis of the at. mass differences of the 2 compds. As_2Se_3 appears to be the 1st published example of a glass which exhibits the limiting Dulong and Petit heat capacity over a sizeable temp. interval before the onset of the glass transition. The lack of correspondence between $T(g)$ and Debye temp. is of considerable importance with regard to the production of ir-transmitting chalcogenide glasses, since it indicates that one may optimize ir-transmission characteristics by using high at. mass components without lowering drastically the upper use temp., i.e., the glass transition temp. TCVL

71:16185r Vapor pressure and thermal stability of arsenic chalcogenides. Kuadzhe, B. M.; Ustyugov, G. P.; Kudryavtsev, A. A. (USSR). *Tr. Mosk. Khim.-Tekhnol. Inst.* 1968, No. 58, 29–32 (Russ). Vapor pressures of liq. As_2S_3, As_2Se_3, and As_2Te_3 at the resp. temp. intervals 720–880, 925–1117, and 1052–1200°K. were measured by using the direct statistical method in a quartz-membrane manometer. The chalcogenides were prepd. from stoichiometric amts. of the resp. elements by heating to 973° in a vacuum of 1×10^{-4} torr directly in the manometer. From the exptl. data, the vapor pressure-temp. relation for each chalcogenide was evaluated. The normal b.ps. 984, 1135, and 1304°K. and the heats of vaporization 19.75, 26.10, and 27.80 kcal./mole were then calcd. for As_2S_3, As_2Se_3, and As_2Te_3, resp. Ds. of overheated vapors were also measured and the mean mol. wts. were calcd. As_2S_3 is a stable compd., the vapors existing in the form of monomeric or dimeric mols. at temps. < b.p. As_2Se_3 and As_2Te_3 are dissocd. considerably under these conditions and the degree of their dissocn. increases from selenide to telluride.

Monika O. Kaparova

71:6728f Saturated vapor pressure of arsenic sulfide, As_2S_3. Kuadzhe, B. M.; Ustyugov, G. P.; Kudryavtsev, A. A. (USSR). *Tr. Mosk. Khim.-Tekhnol. Inst.* 1968, No. 58, 27–8 (Russ). The vapor pressure of realgar, As_4S_4, was detd. at 663–838°K. by using a quartz diaphragm manometer. The results, expressed in mm. of Hg, fit the equation: $\log p = (3637.2/T) + 7.1847$, from which ΔH (vaporization) = 16.6 kcal.

N. D. Haworth

69:20710j Vacuum condensation of arsenic sulfide. Ivakova, R. A.; Spivak, M. M.; Chelokhsaev, L. S. *Tr. Inst. Met. Obogashch., Akad. Nauk Kaz. SSR* 1967, 26, 68–76 (Russ). A vacuum thermobalance is described for detg. the amt. and the crit. temp. of sulfides condensing in vacuo (0.1–0.01 mm. Hg) as a function of temp. and the material of the condensation substrate, the d. of the vapor stream, and the thickness of the condensate layer. The effect of temp. of a Al-foil base on the degree of condensation of As_4S_4 was studied at a residual pressure of 0.5 mm. Hg and a rate of evapn. of 0.005 g./cm.^{2} sec.: starting from 200°, the degree of condensation increased with increasing temp.; above 200°, condensation practically did not occur. An increase in the vapor d., at an evapn. rate of 0.0009–0.0055 g./cm.^{2} sec. and a residual pressure of 0.5 mm. Hg and a condenser temp. of ~50° practically did not alter the degree of condensation. The degree of condensation was sharply affected by the residual pressure. The effect of the thickness of the condensate layer on the degree of condensation was studied at an evapn. rate of 0.0043 g./cm.^{2} sec., a residual pressure of 0.5 mm. Hg, and a temp. of the base of ~10°; during an increase in the condensate from 5.4 to 70 mg./cm.^{2}, the degree of condensation of As_4S_4 practically did not vary (59–54%). The material of the substrate affected only slightly the degree of condensation. Consequently, the most important factors affecting the rate of the process during condensation under moderate vacuum are the temp. of the substrate and the residual pressure in the reaction zone. The appearance of the condensates under the microscope was different with respect to color and to coarseness of the crystals and drops. 36 references.

Jean Plamondon

Thermodynamic properties of gaseous compounds of Group V elements with chalcogen elements. S. I. Gorbov and A. N. Krestovnikov (Inst. of Steel and Alloys, Moscow). *Zh. Fiz. Khim.* 40(4), 930–3(1966)(Russ). Based on the systematization of the spectroscopic data and on the evaluation of the mol. consts. of 2-at. mols. of the chalcogenides of As, Sb, and Bi in the ground electronic state, the tables for the mol. consts. used in the calcns. were compiled. For calcg. the vibrational-rotational components of the thermodynamic functions of the mols. BiSe, BiTe, SbSe, SbTe, BiS, the approxn. method of Maier and Geppert-Maier (*Statisticheskaya Mekhanika*, Moscow: Izd. Inostr. Lit., 1952) was used which is based on the assumption that the levels of the vibrational and rotational energies of two-atom mols. can be described by 2-term equations. The calcns. were made on a digital computer using the mol. consts. and the consts. in the equations for the calcn. of thermodynamic functions of two-atom gases. The energies of the 1st excited states for the mols. BiTe, BiSe, BiS, SbTe, and SbSe are of the order of 25,000–45,000 cm.$^{-1}$, so that up to a temp. of 3000°K. the contribution to the statistical sum of the excited electron states can be neglected. The mols. AsS, AsSe, AsTe, and SbS were calcd. in the approxn. of the rigid rotator-harmonic oscillator. 10 references.

65: 6371h L. Holl

Types of oxidation reactions observed during the course of differential thermal analyses, in air, of sulfurous and arsenious Fe, Co, Ni, Cu, Zn, Ag, and Pb ores. C. Maurel (Lab. Mineral., Paris). *Bull. Soc. Franc. Mineral. Crist.* 87(3), 377–85(1964)(Fr). In the course of differential thermal analysis in air of sulfides and arsenides of Fe, Co, Ni, Cu, Zn, Ag, and Pb, oxidn. of 5 types was observed. These were: (*1*) partial volatilization of the S and As, leaving a sulfide or arsenide more rich in metal, (*2*) total volatilization of the S and As and oxidn. of the metal, (*3*) oxidn. to a sulfate or an arsenate, (*4*) oxidn. and selective volatilization of As, yielding a sulfide in the case of a sulfoarsenide of Ni or Ag, and (*5*) selective oxidn. of one of the 2 metals present in the same mineral.

62: 6193d George H. Chase

Low-temperature heat capacities and entropies at 298.15°K. of sulfides of arsenic, germanium, and nickel. W. W. Weller and K. K. Kelley (U.S. Bur. of Mines, Berkeley, Calif.). *U.S. Bur. Mines, Rept. Invest.* 6511(8), 7 pp.(1964). Exptl. heat capacity data for AsS, GeS, NiS, and Ni_3S_2 were detd. from 50 to 298.15°K. The entropies, $S°_{298.15}$ are 15.18 ± 0.15, 15.77 ± 0.13, 12.66 ± 0.08, and 32.0 ± 0.2 cal./degree mole, resp. The entropies of formation, $\Delta S°_{298.15}$, from cryst. metal and rhombic S are −0.8, +0.7, −2.1, and −4.7 cal./degree mole, resp. C. W. Schuck

Vapor pressure of arsenic and thallium sulfides. R. A. Isakova and V. N. Nesterov. *Tr. Inst. Met. i Obogashch., Akad. Nauk Kaz. SSR* 5, 29–33(1962). The vapor pressure of As_2S_3 was measured by a modified statistical method, in a closed vessel at 350–540°. The relation between the temp. and the vapor pressure is given by $\log P_{mm.} = (-3865.1/T) + 7.118$. Hsiao and Schlechten (*CA* 46, 1321*b*) obtained much lower values. The latent heat and the variation of entropy are 17,683 cal./mole and 19.39 cal./mole degree; these values are independent of temp. in the given temp. range. The b.p. of As_2O_3, 660°, was found by extrapolation. The vapor pressure of Tl_2S was measured by 2 methods: the statistical in the temp. range 800–1030°, and the transfer method, at 700–770°. The results of the 2 methods agreed well; the temp. dependence of the vapor pressure of Tl_2S is expressed by $\log P_{mm.} = -(8820/T) + 8.51$. These results are closer to those of Klanberg and Spandau (*CA* 53, 797*e*) than to those of Shchukhinskii and Kuliev (*CA* 54, 18949*h*). The variation of the free energy of evapn. is 37,610 + 25.74 T; the enthalpy and the variation of entropy are 37.6 kcal./mole and 25.74 cal./mol. degree, resp. 59: 424 Anicia Klein

Thermal decomposition and vapor-pressure measurements on arsenopyrite and an arsenical ore. B. A. Strathdee and L. M. Pidgeon (Univ. Toronto). *Can. Mining Met. Bull.*, 54, 553–7; *Trans. Can. Inst. Mining Met.* 64, 506–10 (1961).—A flotation concentrate from Giant Yellowknife Au ore contg. 24.5% FeAsS and 30.7% FeS_2 was heated to a temp. at which decompn. and distn. took place. The condensate consisted of metallic As and AsS, although analysis of the ore showed that volatile As and S were present in proportion to produce a condensate of As_2S_3 and S. Distn. tests on the mineral arsenopyrite also produced a condensate of metallic As and AsS. This arsenic sulfide gave a distinct x-ray diffraction pattern which was not listed in the A.S.T.M. data file. This sulfide can be produced by heating a mixt. of As and S *in vacuo*. Its chem. analysis corresponds to As_2S_3. The dissocn. pressure of arsenopyrite and the vapor pressures of AsS and As were measured with a quartz "spoon" gauge. The dissocn. pressure of arsenopyrite was compared with the published data for the dissocn. pressure of pyrite to account for the behavior of an arsenical ore during thermal decompn. 56: 9782b C. W. Schuck

Low-temperature specific heat and entropy of sulfides of the Group V elements at 298.1°K. V. A. Romanovskii and V. V. Tarasov (D. I. Mendeleev Inst. Chem. Technol., Moscow). *Fiz. Tverdogo Tela* 2, 1294–9(1960).—The molar sp. heats of cryst. As_2S_3, Sb_2S_3, and Bi_2S_3 at 65–300°K. were detd. by means of an improved Lange-Harteck adiabatic calorimeter. The sp. heats were extrapolated to 0°K. according to Tarasov's formulas for chain structures (*CA* 56, 741) and the abs. entropies of the sulfides at 65 and 298.1°K. were calcd. by graphic integration.

56: 8022d E. Jozefowicz

Specific heat of trisulfides of arsenic, antimony, and bismuth in connection with their structure and physicochemical properties. V. A. Romanovskii and V. V. Tarasov. *Fiz. Tverdogo Tela* 2, 1287–93(1960).—A crit. review on the structure and chem. bonds in these compds., followed by comparison of the theoretically computed and exptl. sp. heats.

56: 791i M. Shelef

The low-temperature specific heat and the entropy at 298.1°K. of sulfides of Group V elements. V. A. Romanovskii and V. V. Tarasov (D. I. Mendeleev Chem.-Technol. Inst., Moscow). *Fiz. Tverdogo Tela* 2, 1294–9(1960).—Measurements were made with an adiabatic calorimeter on orpiment (As_2S_3), antimonite (Sb_2S_3), and cryst. Bi_2S_3 at 10° intervals from 65 to 300°K. The entropies was calcd. from the data by graphical integration.

B. A. Stevens

Specific heat and heat content of compounds of cadmium, mercury, arsenic antimony, and bismuth. A. N. Krestovnikov, M. S. Vendrikh, and E. I. Feigina. *Sbornik Nauch. Trudov Moskov. Inst. Tsvetn. Metal. i Zoloto i Vsesoyuz. Nauch. Inzhener.-Tekh. Obshchestvo Tsvetnoi Met.* 1957, No. 28, 233–58.—A crit. evaluation of bibliographic data on the sp. heat and heat content of CdO, CdS, $CdCl_2$, HgO, HgS, Hg_2SO_4, $HgCl$, $HgCl_2$, As_2S_3, As_4O_6, As_2O_5, Sb_4O_6, Sb_2O_4, Sb_2O_5, Sb_2S_3, $SbCl_3$, Bi_2S_3, and Bi_2O_3 is given. 25 references. From *Referat. Zhur., Met.* 1958, Abstr. No. 14199.

54: 11622c K. L. C.

Affinity of metals for sulfur. E. V. Britzke and A. F. Kapustinskii. *J. Phys. Chem.* (U. S. S. R.) 5, 85–90 (1934); *cf. C. A.* 25, 1420; 26, 2637, 2638, 2914, 3428.—The heats of formation of various sulfides from the metal and rhombic S were detd. as follows: FeS 18.0, SnS 18.5, Sb_2S_3 38.3, As_2S_3 (amorph.) 9.6, As_2S_3 (cryst.) 28.9, As_2S_3 (amorph.) 34.5, Cu_2S (cryst.) 20, $As_2O_3 \cdot SO_3$ 23.62, $As_2O_3 \cdot As_2O_5$ —24.5. A table is given showing that as the radii of the metal ions increase the electrolytic dissocn. consts. of sulfides decrease while the thermal dissocn. consts. increase. Determination of the heat of formation of disulfides and trisulfides of arsenic. E. V. Britzke, A. F. Kapustinskii and L. G. Chentzova. *Ibid.* 91–6 (1934); *cf. C. A.* 27, 4098.—On the basis of data obtained from the combustion of As_2S_3 and As_2S_5 with the formation of SO_3 and a mixt. of As_2O_3, $As_2O_3 \cdot As_2O_5$ and $As_2O_3 \cdot SO_3$, the heats of formation of solid As_2O_3 and As_2S_5 from solid As and rhombic S are calcd. as 28.9 and 34.7 Cal., resp. Determination of the heat of formation of double compounds of pentoxide and trioxide of arsenic, and the heat of formation of sulfate of arsenic. *Ibid.* 97–102(1934).—The heats of formation of $As_2O_3 \cdot SO_3$ from solid As_2O_3 and gaseous SO_3 and of solid $As_2O_3 \cdot As_2O_5$ from solid As_2O_3 and solid As_2O_5 are 23.03 and —24.5 Cal., resp. The heats of soln. of As_2O_3 and As_2O_5 in NaOH (0.53 *N*) are +9.61 and +63.23 Cal., resp. F. H. R.

Affinity of metals for sulfur. III. Heats of combustion and formation of the sulfides of arsenic and the compounds $As_2O_3 \cdot As_2O_5$ and $As_2O_3 \cdot SO_3$. E. V. Britzke, A. F. Kapustinskii and L. G. Chenzova. *Z. anorg. allgem. Chem.* 213, 58–64(1933); *cf. C. A.* 26, 3423.—The heats of formation of As_2S_3 and As_2S_5 are about 135 cal./g. and 140 cal./g., resp. The heats of combustion of As_2S_3 and As_2S_5 to give $As_2O_3 \cdot SO_3$ are about 3.6 and 1.59 cal., resp., and to give $As_2O_3 \cdot As_2O_5$ about 1.19 and 0.404 cal., resp.

The affinity of metals for sulfur. II. Thermal dissociation equilibria of the sulfides of silver, copper and arsenic. E. V. Britzke and A. F. Kapustinskii. *Z. anorg. allgem. Chem.* 205, 95–112(1932).—With a new direct process, based on the permeability of heated Pt to H_2, expts. were made to det. the equil. between H_2 and Ag_2S and the dissocn. pressure, max. work and heat effects of the formation of Ag_2S in the temp. region 912–1067° were calcd. Similar calcns., based on the gas current process (*cf. C. A.* 25, 1430), were made for Cu_2S from 730° to 875°. With V. Meyer's and W. Nernst's process, the vapor d. of As_2S_3 was detd. from 830° to 1140° and of As_2S_5 from 755° to 1075°; the degree of dissocn. as well as the consts. of the dissocn. and the heat of formation of As_2S_5 were calcd. 26: 3428 M. McMahon

Thermochemistry of sulfides of antimony, arsenic, bismuth, cadmium, tin and iron. E. V. Britzke and A. F. Kapustinskii. *Tsvetnie Metal.* 1931, 1147–50; *cf. C. A.* 25, 1420.—The equil. consts. were detd. at different temps. for the reduction of sulfides of Sn, As, Bi, Cd, Sb and Fe with H. From these consts. and the values of the dissocn. const. of H_2S previously detd. by Preuner, Schupp, Randall and Bichowsky the dissocn. pressures of the sulfides are calcd. The logarithms of the dissocn. pressures are plotted against the reciprocals of abs. temps., and the following equations obtained for the vapor pressures of S at different temps.: For FeS, $\log P_{S_2} = -(14329/T) + 5.80$; SnS, $\log P_{S_2} = -(15430/T) + 8.10$; CdS, $\log P_{S_2} = -(15130/T) + 3.02$; Bi_2S_3, $\log P_{S_2} = -(16270/T) + 14.25$; Sb_2S_3, $\log P_{S_2} = -(12660/T) + 8.95$; As_2S_3, $\log (P'^{3}_{S_2} P_{As_4} / P'^{2}_{As_2}) = -(312000/T) + 53.8$. The results were confirmed by direct measurements. From the above equations the heats (in cal.) of formation of sulfides from diatomic (gaseous) S and the solid metals are: $2Fe + S_2 = 2FeS + 65460$; $2Sn + S_2 = 2SnS + 70520$; $2Cd + S_2 = 2CdS + 69140$; $2Bi + 1\frac{1}{2}S_2 = Bi_2S_3 + 111540$; $2Sb + 1\frac{1}{2}S_2 = Sb_2S_3 + 86490$; $2As + S_2 = As_2S_3 + 51430$. By introducing the correction for the heat of condensation of diatomic S to rhombic S the heats of formation of the sulfides from rhombic S and solid metals are: $Fe + S_2 = FeS + 17980$; $Sn + S_2 = SnS + 20510$; $Cd + S_2 = CdS + 19800$; $2Bi + 3S_2 = Bi_2S_3 + 67200$; $2Sb + 3S_2 = Sb_2S_3$ (black) + 42500; $2As + 2S_2 = As_2S_3 + 21930$. From the results thus obtained and the heats of formation of H_2S obtained by Berthelot (*Ann. chim. phys.* [5], 22, 429(1881)), and of the oxides of the metals from Landolt and Börnstein (Physikalisch-Chemische Tabellen, Berlin, 1923), the heats of reactions representing roasting of the sulfides are: $2[FeS] + 3.5(O_2) = [Fe_2O_3] + 2(SO_2) + 209540$; $[SnS] + 1.5(O_2) = [SnO] + (SO_2) + 115500$; $[CdS] + 1.5(O_2) = [CdO] + (SO_2) + 112500$; $[Bi_2S_3] + 4.5(O_2) = [Bi_2O_3] + 3(SO_2) + 278500$; $[Sb_2S_3] + 4.5(O_2) = [Sb_2O_3] + 3(SO_2) + 328400$; $(As_2S_3) + 3.5(O_2) = [As_2O_3] + 2(SO_2) + 271370$.
26: 2634 B. N. Danilov

A study of the thermal dissociation of the disulfide and trisulfide of arsenic. E. V. Britzke, A. P. Kapustinskii and L. G. Chentsova. *J. Chem. Ind.* (Moscow) 8, No. 19, 1–7(1931).—The vapor d. of As_2S_3 is detd. from 760° to 1030°. The compd. begins to dissoc. into its elements between 781° and 830° and is completely dissocd. at 1076°. The heat of formation from its elements is 19,200 cal. The vapor d. of As_2S_5 is detd. from 820° to 1150°. It is estd. that dissocn. occurs at 800–1000°. As_2S_5 is less stable than As_2S_3. 26: 2634 H. M. Leicester

Industrial Processes: "Recovery"

84: 77229e Pilot-plant testing of the vacuum thermal process for the treatment of polymetallic mattes. Khobdabe= rgenov, R. Zh.; Nesterov, V. N.; Isakova, R. A.; Ibragimov, P. T.; Shendyapin, A. S. (USSR). *Tsvetn. Met.* 1975, (11), 27 (Russ). Treatment of matte from Pb conc. smelting and decoppering of crude Pb, contg. Pb 8–15, Zn 5–10, Sb 0.3–0.5, and As 0.8–1.5%, gave low-grade, impure Cu. Lab. expts. showed that Pb and Zn could be volatilized rapidly in a vacuum app. In pilot plant tests the temp. was 1050–1150°, treatment time 6 hr, initial pressure 160, and after 1 and 2 hr of treatment 5 and 3 torr, resp., and initial bath depth 350 mm. The treatment residue contained Pb 2, Zn 0.75, Sb 0.03, and As 0.14%, and the cyclone condensate Pb 63.8, Zn 23.3, Sb 0.3, and As 1.26%. The recovery was Pb 90.5, Zn 81.2, Sb 83.4, and As 83.2%. The condensate was a readily flowing powder.

E. M. Elkin

84: 20739a Recovery of arsenic and tin from gases being formed during the fuming process of a tin-containing raw material. Terebenin, A. N.; Bykov, A. P. (Central Scientifi= -Research Institute of the Tin Industry) U.S.S.R. 484,584 (Cl. B01d), 25 Sep 1975, Appl. 1,734,194, 04 Jan 1972. From *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* 1975, (35), 15. As [7440-38-2] and Sn [7440-31-5] were recovered from gases by passing the gases through the dust-collecting filters at a temp. above the dew point of As_2O_3. To make possible the sep. recovery of As and Sn sublimates, the Sn sublimate was entrapped when the content of O in gases was 5.8–6.0 vol.%.

84: 123757g Purification of arsenic trioxide and apparatus therefor. Iwai, Hideichiro; Omura, Koji (Mitsui Mining and Smelting Co., Ltd.) Japan. Kokai 74 26,267 (Cl. 15 B71), 15 Mar 1974, Appl. 72 70,415, 15 Jul 1972; 4 pp. As_2O_3 contg. Pb, Sb, Hg, Se, etc., is mixed with gypsum or silicates to prevent melting, heated in a stream of air to sep. from Pb and Sb, filtered at 150–250° into a bag-filter to collect As_2O_3, and then at a lower temp. into a 2nd bag filter to collect the impure As_2O_3. Thus, 97.0% pure As_2O_3 contg. Pb 0.10, Sb 0.12, Hg 0.20, and Se 0.08% (2 kg) was mixed with 1 kg gypsum, introduced into a drum at 500° by a screw-conveyer, heated for 1 hr, and the vapor was swept by air to contain 120 g/m³ into the 1st bag filter of glass fiber at 150–250° and into the 2nd of Tetron fiber at 90–100°. The yield in the 1st bag filter was 1850 g of >99.5% pure As_2O_3 contg. Pb 0.002, Sb 0.01, Hg 0.0005, and Se 0.0015% and in the 2nd bag filter the resp. values were 70 g, >85, 0.12, 0.60, 0.16, and 0.40%, resp.

K. Kodama

84: 28615z Conversion of polymetallic raw material. Isakova, R. A.; Nesterov, V. N.; Chelokhsaev, L. S.; Nesterov, P. V.; Mel'nikov, S. M.; Volodin, V. N.; Zrazhevskii, P. D. (Institute of Metallurgy and Ore Beneficiation, Academy of Sciences, Kazakh S.S.R.) U.S.S.R. 355,045 (Cl. C 22b), 22 Jun 1973, Appl. 1,689,488, Appl. 30 Aug 1971. From *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* 1973, 50(28), 82. The conversion of metallic raw material contg. metal sulfides which are volatile at >500°, e.g. As and Sb sulfides, by distn. oxidizing roasting in a fluidized bed is described. To intensify the oxidn. of volatile metal and sublimation of the oxidn. products and to increase the purity of the products, the roasting was carried out at a residual pressure in the furnace from 1 to 100 mm Hg, and a gas contg. free O was fed into the polymetallic raw material layer in an amt. necessary for obtaining only lower acids.

80: 62352b Preparation of sublimates with low arsenic content during the fuming of lean tin-containing raw material. Terebenin, A. N.; Bykov, A. P. (USSR). *Tsvet. Metal.* 1973, (8), 34–6 (Russ). The gas phase sepn. of Sn and As was studied during the fuming of a lean conc. contg. Sn 3.3, As ≤1 (as arsenopyrite), Fe ~23, and S 22–4%, and Cu, Zn, and Pb. Passing the fume- and dust-laden gas through a wet scrubber gave 99.15% recovery of 0.346 μ aerosol particles contg. Sn 55.6 and As 5.7%. The Sn occurred chiefly as SnO_2 and to a lesser degree as SnO, SnS, and Sn; and the As chiefly as As_2O_3 and partly as sulfides. Zn and Pb arsenates, As, and As_2O_5. When the gas was passed at 260–300° through a bag house provided with metal cloth filters and then through a condenser at 20–30°, the filter bag dust contained Sn 53 and As 1.8%, and the condenser sublimate contained Sn 0.03–0.12 and As ~70%. Increasing the bag house temp. to 350–80° decreased the As concn. in the dust to 0.6–0.8%, but required an auxiliary app. The mechanism of As volatilization and catalytic oxidn. of As_2O_3 by Fe oxides is discussed.

E. M. Elkin

80: 28953p Apparatus for refining arsenous acid by gas flow-type roasting. Yamamoto, Yoshihisa; Hayashida, Morio (Furukawa Mining Co., Ltd.) Japan. 73 23,796 (Cl. C 01b), 16 Jul 1973, Appl. 70 40,369, 12 May 1970; 2 pp. An app. is described for producing As_2O_3 from stack dusts and residues by roasting them in a stream of hot gases without overheating and causing the formation of As_2O_5 and nonvolatile As compds. Thus, gases at 300–700° from burning a fuel are fed into the lower end of an inclined conduit having an adjacent feed for the As-contg. material. The hot gases cause the As_2O_3 to sublime during roasting and transport the remaining solids and As_2O_3 to a separator where the solids are removed, and the As_2O_3 is transported to a recovery vessel where it condenses.

78: 86597v Feasibility of producing technical arsenic trioxide from arsenic-containing tin industry dusts. Terebenin, A. N.; Bykov, A. P. (USSR). *Tsvet. Metal.* 1972, (7), 31–2 (Russ). In lab. expts. on As_2O_3 recovery from Sn smelter flue dust, heating the dust in a current of air for 30 min at 500–600° gave a condensate contg. 98.0–9.5% As_2O_3 with condensation efficiency 97–9%. The residue contained As 7–10 and Sn 3–4%. Raising the temp. >600° did not affect the volatilization and made possible formation of As_2O_5 and nonvolatile compds.

E. M. Elkin

69: 4041m Washing and cooling of roasting gases containing arsenic. Kartenbeck, Werner; Hennenberger, Karl H. (Nord-deutsche Affinerie). Ger. 1264422 (Cl. C 01b), 28 Mar 1968, Appl. 07 Dec 1965; 3 pp. A process which avoids As_2O_3-incrustations is described. Mech. and elec. cleaned gas was sprinkled continuously with circulating H_2SO_4 (45–53° Baume). To keep the concn. const., the cooling tower was fed with ~10% H_2SO_4. By direct evapn. the SO_2-contg. gases were cooled from 300° to 80–110° and the acid was concd. and heated to ~100°. At this temp. the soly. of As_2O_3 is ~17 g./l. Therefore, the As_2O_3 from the gases is not dissolved in the acid but ppt. in easily filterable form. The As_2O_3-free cooling acid was recirculated.

Sigrid Ebeler

64: 31162w Treatment of electrolytic copper refining slimes. Svante Mellgren, William R. Opie, and Lamar D. Coffin (to American Metal Climax, Inc.). U.S. 3,288,561 (Cl. 23-98), Nov. 29, 1966, Appl. May 5, 1964; 2 pp. The slimes are treated with Cl in a bath of molten alkali or alk. earth chlorides, esp. a eutectic mixt. (I) of KCl and NaCl, and the volatile chlorides of Se, Te, Sb, As, and Sn are condensed and recovered in conventional ways. The m.p. of the bath can be reduced by addn. of $AlCl_3$. A reducing agent (CO) helps the action. Thus, 500 g. decopperized slime contg. Se, Te, Sb, Sn, Pb, and noble metals was added to 1700 g. molten I at 750°. Cl (250 g.) was passed in for 2.5 hrs. with agitation by a quartz impeller. The volatile chlorides were recovered in H_2O scrubbers and the residue treated to recover the remaining metal values.

K. J. Durant

Extraction of arsenic from gold-arsenic concentrates by a vacuum-heat method. R. A. Isakova, L. S. Cheloksaev, L. P. Ugryumova, and A. L. Tselt. *Tr. Inst. Met. i Obogashch., Akad. Nauk Kaz. SSR* 13, 28–42(1965)(Russ). The possibility of extn. of As from Au-As concentrates by vacuum-heat distn. was studied. Complete extn. of As from the concentrates was achieved at 500°, residual pressure 1–10 mm., height of concentrate layer 10–15 mm., time 15 min. From *Ref. Zh., Khim.* 1966 (4), Pt. I, Abstr. No. 4V14. 65: 3711b MVRK

Attempts to utilize pyrite wastes in the Peoples Republic of Poland. Wilibald Pajak and Jan Cebula. *Neue Hutte* 10(12), 732–5(1965)(Ger). The compn. of Polish pyrite wastes is: Fe 40–50, Zn 3–8, Pb 0.5–2, S 3–8, CaO 2–5, MgO 0.8–1.5, SiO_2 1.5–4, Al_2O_3 0.15–1.1, As 0.2–1%. Expts. are described for mixing pyrite wastes with iron ore and with calamine ore (probably hydrous Zn silicate) and with $CaCl_2$ as a charge with coke breeze in a rotary kiln. There is a tendency for Zn, As, and Pb to sep. and to form an Fe silicate slag having higher Fe content than the charge. Pelletized flue dust from the manuf. of H_2SO_4 from pyrites contains As 1–5 and Pb 6%. When treated with a H/steam mixt. at 500–1000° in a furnace much of the As is volatilized. If the pellets are treated with Cl, Cu, and Zn sep. as volatile chlorides. 64: 15557h Frank C. Norris

Treatment of anodic sludges from copper electrolysis. American Metal Climax, Inc. (by James E. Hoffmann and Dominic C. Cusanelli). Ger. 1,201,069 (Cl. C 22b), Sept. 16, 1965; U.S. Appl. Nov. 20, 1963; 4 pp. In a process for working up anode sludges contg. Se, Te, Sb, Sn, or As, sep. or together, the sludges are chlorinated at >300° to form the volatile chlorides of the elements contained in the material, and these chlorides are collected. Preferably, the chlorination is effected with 0.3–0.7 kg. gaseous Cl per kg. of the sludge. In the presence of a reducing agent, e.g. coke or CO, the Cl:CO ratio is ~20:1–1:1. The sludges are preferably treated in the form of agglomerates contg. 3.5–10% of an inert binder, e.g. bentonite. The agglomerates may be prepd. with 12.5–17.4% H_2O, and then dried. Chlorination is preferably effected in a reaction chamber into which excess Cl is passed through a 2nd inlet in the upper part of the chamber so that Cl is contacted with the volatile chlorides before these are collected. 64: 3316 Friedrich Epstein

Sublimation of arsenic from arsenopyrite ore of the Tsansk deposit and condensation of its vapor. V. G. Rukhadze and G. N. Zviadadze. *Soobshch. Akad. Nauk Gruz. SSR* 34(1), 127–34(1964). The Tsansk deposit contains arsenopyrite ore with very small amts. of realgar and orpiment. It consists of quartz orpiment veins cutting the schist country rocks. Production of metallic As by sublimation has certain advantages over thermal redn. of the As anhydride with C; single-stage production directly from ore, simpler condensation, and better sanitary conditions. The evapn. of As from ore and concentrate is similar. It is intense at ≥700°. Increase of temp. >725° affected little the evapn. of the As. The evapn. of S did not affect the process of As extn. because the condensation of it (in the form of yellowish brown film) occurs in the colder part of the condenser sep. from the As condensate. The Tsansk ore, in addn. to As, S, and Fe, contains Se, Bi, Au, and Ag. During heating of ore the Se evapd. very little, the Bi evapd. fully, and Au and Ag coned. in the residue. The coned. metallic As contained the following impurities: S 0.51, Se traces, Bi 0.18, Sb 0.012, and Cu 10^{-4}%. 61: 6672e BLJR

Separation of antimony from arsenic. Norddeutsche Affinerie (by Wilhelm Shaefer). Ger. 1,169,427 (Cl. C 01b), May 6, 1964, Appl. Aug. 2, 1962; 2 pp. Pure white As was obtained from As- and Sb-contg. products, i.e. flue dust from Ni roasting was treated with an oxidizing acid (H_2SO_4 or HNO_3), was heated to 600° to free the As in the form of As_2O_3, at the same time Sb oxidized from Sb_2O_3 to Sb_2O_4, and the As sublimed. Addn. of sand prevented sintering of the furnace contents. Quick heating to the sublimation temp. is important. Thus, 16 kg. flue dust of 0% As and 40% Sb was used, with 8 kg. of sand, and 31 kg. arsenic acid was heated for 3 hrs. in a furnace plus 1 hr. more for sublimation; in a receiver 8.2 kg. of As with 71.5% As was collected. The furnace residue held 0.9% As and 23.4% Sb. 61: 3959d Olga Rummel Fry

Chlorinating roasting of oxidized ores. Chlorine exchange between calcium chloride and the oxides of some metals. Ana Moscovici and A. Cornea (Inst. Chem. Res., Bucharest, Romania). *Rev. Chim.* (Bucharest) 14(11–12), 661–8(1963). The influence of diverse parameters on the chlorinating roasting of a mixt. of pyrite ash, contg. nonferrous metals, with $CaCl_2$, in the form of dry pellets, was investigated to det. the optimum volatilization conditions. The pyrite ash (≥60% −0.071 mm.) contained Fe 48–55, S 1.5–2.0, Cu 0.36, Zn 0.59, As 0.28, SiO_2 15.72–18.62, Al_2O_3 3.81–5.2, MgO 0.32–2.41, CaO 0.33–2.63%, Ag 530–750, Au 36–47, Ge 20–5 g./ton. The $CaCl_2$ was added as a satd. soln. at a proportion of 5–15%, and the mixt. was pelletized (2.5 mm. in diam.) and dried to 1–5% moisture. The pellets were roasted in a fireclay tube of a vertical elec. furnace, the charge being 200 g. pyrite ash. The roasting temp. was 800–1150°. The volatile reaction products were entrained in a 10–200 l./hr. air current and trapped in condensers and water flasks. The agglomerated ferrous residue was eliminated from the bottom of the tube. Addnl. parameters varied were the S content (2–8%), the effective roasting duration, and the pellet diam. At S 2, $CaCl_2$ 8%, air 200 l./hr., and 2 hrs. roasting, the volatilization yields of Ge, Au, Ag, and As increased with the roasting temp.; the increase for Au and As was slower. The volatilization yields of Cu and Zn increased with the temp. up to 1000–1100°; the Zn yield levelled off at an approx. const. value, while the Cu yield decreased considerably at higher temps. Under the same conditions, except for the S content, which was 3–8%, the volatilization yields increased with the roasting temp. up to 5% S and decreased considerably at higher S contents, except the As yield, which increased with both the temp. and the S content, passing through a min. at 1000°. At S 5%, air 100 l./hr., duration 2 hrs., and varied $CaCl_2$ addns. (5–15%), the volatilization yields increased with the temp. and with the $CaCl_2$ content, but in the case of Ge the yield decreased strongly at 15% $CaCl_2$ at >1100° to values which were not below those obtained at 5 and 8% $CaCl_2$. The time factor had a strong effect on the completion of the volatilization of all metals, but esp. on that of the Ge, Zn, Cu, and Ag, and to a smaller degree on that of Au; the yields did not increase when the roasting duration exceeded 4 hrs. at all temps. The air flow rate had no effect on the volatilization yields, and only in the case of As did the yield increase from 66% at 10 l./hr. to 76.5% at 200 l./hr. air. The increase of the size of the pellets from 8 to 15 mm. diam. did not affect the As yield, decreased the Au and Cu yields somewhat, and decreased the Ge, Zn, and Ag yields considerably. The volatilization yields were very low when the pellets were prepd. by extrusion, indicating that the porosity had an important role in the volatilization process. The results of the process were recovery of the nonferrous metals from the ash (6–8%) as volatile dusts and recovery of the Fe (97%) by transformation into a well agglomerated residue, contg. Cu 0.1, Zn 0.12, As 0.08, Cl 0.09, and S 0.03%. Thermodynamic considerations were presented, showing that the process took place by decompn. of the $CaCl_2$ following reactions with S oxides and O or with SiO_2 and Al_2O_3, the resulting Cl reacting with the nonferrous metal compds. Examn. of the free enthalpy values indicated the following decreasing order in the tendency to chloride formation: Ag(Au), Pb, Cd, Zn, Cu, Fe, Ge, As. Under oxidizing and moist conditions the Fe and in part the Cu chlorides were transformed into the oxides, the volatile dust contg. only 1% $FeCl_3$. These considerations also showed that the temp. increase up to 1000° favored the chlorination process, with the exception of Zn, Pb, and Ni, where the $\Delta G_T°$ increased strongly above 1000°. An optimum ratio was found between the percent S and percent $CaCl_2$ in the charge, at a value 1.4, which represented a slight $CaCl_2$ excess over the theoretical ratio 1:3.47. This confirmed that the reactions between the $CaCl_2$ and the sulfurous gases were preponderant. The excess was necessary for eventual double exchange reactions and for consumption of the sulfurous gases which may det. a reducing atm. in the pellet interior, favoring chlorination of Fe. 18 references. 60: 15424e M. Lapidot

Kinetics of distillation of zinc, lead and certain rare elements in the treatment of metallurgical dusts by the pyroselection method. A. A. Babadzhan, V. M. Zhukovskii, K. F. Zaponova, and E. A. Vetrenko. *Tsvetn. Metal.* 36(11), 20–2(1963). The dust, recovered in the waste-heat boilers and Cottrell precipitators of shaft furnaces, was charged in alternate layers with coke into converters, covered with liquid matte, and blown. Of the substances volatilized, Cu, Fe, SiO_2, Al_2O_3, and a part of the S were carried over mech., and the rest were distd. and sublimed. Volatilization-time curves showed that the order of increasing volatilization the elements is Sb < As < Zn < Cd < Pb < In < Se + Te. The volatilization degree at the end of 14 hrs. was Se + Te 100, and Sb 53%. The sublimate was treated readily by hydrometallurgical methods. 60: 8920b E. M. Elkin

Distillation of arsenic from zinc and lead arsenates during sulfatization of metallurgical dusts. L. S. Getskin, V. F. Larin, and V. V. Yatsuk. *Sb. Nauchn. Tr. Vses. Nauchn.-Issled. Gorno Met. Inst. Tsvetn. Metal.* 1962(7), 31–5. Expts. were conducted on sulfatization of As-contg. Pb dusts in a fluidized layer furnace with concd. H_2SO_4 and an atm. of O-enriched air. The O concn. in the air-O mixt. was 21–30%. With 21% O, As distn. was 78.0% of the initial content in the dust for 60 min. at 350°; for the same time at 30% O it was 87.5%. At 400° for 60 min. it was 80 and 84%, resp., for 21 and 30% O. Elimination of As comprises decompn. of arsenates with H_2SO_4, redn. of the thus formed arsenic acid to arsenous acid, and sublimation of As_2O_3 formed from thermal dissocn. of the arsenous acid. The chemistry of the process depends considerably on the concn. of the H_2SO_4 used. From *Ref. Zh., Met.* 1963, Abstr. No. 20J222. 59: 6046h MVRM

Separation of arsenic. Compagnie Belge-Continentale des Minerais et Metaux S.A. "Contimine." Ger. 1,135,357, (Cl. 18g), Sept. 13, 1962, Appl. Nov. 4, 1960; 4 pp. As can be extd. from ores, from metallurgical by-products, or cinders with reducing gases, HCl, and steam; both residues and gases are preheated to 150–700°. Time of contact is 6–10 min. Thus, a pyrite cinder contg. 57.4% Fe, 0.62% As, and the rest SiO_2, S, Pb, Al, Cu, Cd, and Zn is passed countercurrently to a gas mixt. contg. 85% burner gas (inert gas and steam), 8% reducing gas (coal gas), and 7% HCl. At 150° the gases reduce As(V) to As(III), finally producing $AsCl_3$, which is later sepd. by any dry or wet sepn. method. 58: 3136g Klara Weiner

Treatment of sulfide minerals. Patrick J. McGauley (to Chemetals Corp.). U.S. 3,053,651 (Cl. 75–116), Sept. 11, 1962, Appl. Jan. 21, 1958; 10 pp. FeS, is rendered sol. in dil. H_2SO_4 by lowering the ratio S/Fe to <1 while the nonferrous sulfides are kept insol. The main stages of the process are: (*1*) roasting the mixt. at a temp. below the m.p. to expel excess S; (*2*) activating the calcine by addn. of a small amt. of Fe and roasting, whereby the S/Fe ratio is lowered to <1; (*3*) leaching with 10% H_2SO_4, by which Fe goes into soln., while the nonferrous sulfides remain as insol. residue; (*4*) decompn. of $FeSO_4$ by oxidn. and hydrolysis or by the action of pyrites, with ferric hydroxide or oxide as end product; (*5*) oxidn. of the residue to sulfates in a pressurized slurry at moderate temp., the metals (Pb, Au) Cu, Ag, Sn, Hg, etc.; Zn, Cd; Ni, Co; etc.) pptd., by groups, as sulfides, then treated by conventional methods. Some advantages of the process are: (*1*) recuperation of S (Se, As) to nearly 90%, as H_2S and SO_2; (*2*) use of pyrite as fuel for decompn. of $FeSO_4$; (*3*) use waste solns. and pyrites from Cu-recovery plants; (*4*) no extra reagents are introduced, and the products can be recycled in the continuous process. 58: 3135c B. Brajnikov

Behavior of the main components of speise during converting. N. I. Mikhailov, V. D. Ponomarev, O. G. Miller, and M. A. Abdeev. *Met. i Khim. Prom. Kazakhstana, Nauchn.-Tekhn. Sb.* 1961, No. 1, 16–22. The possibility of converting speise and the behavior of its main components was studied under lab. conditions. Expts. were conducted on an app. consisting of a Silit furnace and a covered graphite or corundum crucible. The initial speise compn. was (in %): Cu 27.10, Pb 4.5, Fe 36.70, Zn 2.16, S 2.04, As 28.70. The speise was converted with an addn. of quartz at 1200° and an air consumption of 1 l./min. In converting speises, they are coned. in respect to Cu (>90%) by oxidn. of Fe arsenide. Pb is practically completely removed (blowing out reduces its content to practically zero). An increase in the content of As and Zn indicates that their compds. are very stable; they are only more intensely oxidized by achieving 75–80% Cu in the coned. speise. The Cu content in the final product was 97%; Zn, Sb, Pb, and Fe ≤0.01%. The obtained sublimates are a high-As concentrate contg. As 69.60, Pb 6.23%, *et al.* More intense sublimation of Pb occurs with higher air consumptions. The optimum temp. for speise conversion is 1150–1250°. From *Ref. Zh., Met.* 1962, Abstr. No. 1G192. CA

Examination of arsenic-gold concentrates. P. S. Gotkin and S. M. Barakov. *Sb. Nauchn. Tr., Kazakhsk. Gorno-Met. Inst.* 1960, No. 19, 86–92. The flow sheet for treatment of As-Au concentrates which warrant recovery of As, S and other elements is: Calcination at 750–800° for 45 min.; leaching the calcine in H_2SO_4 (50 g./l.) for 40 min. at 60°; cyanidation of residue in NaCN (0.05–0.1%) for 24 hrs. with the ratio liquid:solid = 2:1; extraction of Au 91–2%. As is recovered by sublimation. 57: 9506c Eran N. Davidenko

Roasting of fine-grained arsenic-bearing pyrites in a whirled wave of flue dust. Metallgesellschaft A.-G. (by Franz Schytil and Hubert Krollmann). Ger. 1,116,251 (Cl. 18a), Nov. 2, 1961, Appl. July 21, 1959; 2 pp. After flotation, pyrites contg. 0.35% As and 0.48% S were introduced at the bottom of a roasting furnace at rate of 16 tons/sq. m./day. The temp. in the lower part of the furnace is kept at 500° and in the upper part at 800–900°. The air mass is introduced at a rate which produces primarily magnetite in the roasting product. By means of a cyclone separator at 800°, 80% of the by-products with As content of <0.05% is extd. The residue, passing into a steam drum onto a hot gas electrofilter, contains a higher percentage of As. 57: 3118i Helmut Thielsch

Multiple-hearth roasting of pyrite with recovery of waste heat, arsenic, antimony, and lead. Horst Guenter Dietrich. *Freiberger Forschungsh.* B64, 43–55(1962).—The multiple-hearth furnace was studied to raise capacity, increase the efficiency of S removal (with As), and recover heat from the roaster gas. Improved rabbling arms of castable Cr steel were designed to resist corrosion, bending, and breakage. Gas offtake from the 4 top hearths replaced use of the top hearth only. The hot gas, rich in SO_2, passes through a waste-heat boiler, losing half its heat to steam, and some of the partly cooled gas returns to the 4 hearths below the top 4. Fresh air goes down the center shaft that carries the rabbles and enters the 3 bottom hearths to finish calcination and leave a calcine with only 0.5% S. As_2S_3 boils off at 707° and the furnace temp. reaches 800–950°; Sb_2S_3 b. 857°; PbS b. 1280° but evaps. at lower temps. The capacity of the furnace to remove S was as high as 124–150 kg. S/sq. m. in 24 hrs. Net heat recovery was 48%. The removal of As was 96%, that of Sb 94%, Pb 85%, and S 99%. The multiple hearth can thus use cheap grades of FeS, with high As and Sb and produce high-grade Fe ore. 56: 15230g O. C. Ralston

Recovery of rare metals from the dusts of copper-smelting plants. G. N. Sosnovskii. *Tr. Altaisk. Gorno-Met. Nauchn.-Issled. Inst., Akad. Nauk Kazakhsk. SSR* 11, 60–4(1961).—The sublimate obtained from the fine dust evolved in production of Cu was further treated by granulation and roasting in a furnace with a fluidized bed. For granulation, concd. H_2SO_4 was used, its ratio to the sublimate being 1:1. During the sulfatization of granules in a furnace with a fluidized bed at 300°, Pb is sulfatized to 98–100, Cd to 93–8, and Zn to 97–8%. In, Tl, and Te remain in the sulfate product, while 85% of the As and 90% of the Se volatilize being collected in a bag filter. 56:13275a J. P. Tyroler

Roasting arsenic-containing sulfidic ores. Bolidens Gruvaktiebolag (by Ernest Gustav Boholm). Swed. 176,024, Sept. 25, 1961. Appl. Apr. 30, 1954. The ore, e.g., FeS_2, is treated in 2 furnaces: a sublimation furnace and a roasting furnace. The ore is introduced under nonoxidative conditions into the sublimation furnace, where the heat derived from hot, roasted ore which arrives from the roasting furnace is used to expel the bulk of the As (or As_2O_3) by sublimation. In the roasting furnace, the ore which is essentially free from As is maintained as a fluidized bed and roasted by the introduction of O-contg. gases, e.g., air. The connecting passages between the 2 furnaces are very wide. The As_2O_3 is condensed and recovered for com. purposes. 56:12599g Werner Jacobson

Distillation and recovery of selenium and arsenic during the sulfation of metallurgical dusts. L. S. Getskin and V. P. Savraev. *Zhur. Prikkl. Khim.* 34, 2398–2403(1961).—The degree of distn., *x*, of Se and As in the sulfation of metallurgical dusts was studied with an industrial dust contg. Pb 51.1, Zn 13.6, Se 0.24, and As 3.3%. The dust, granulated with concd. H_2SO_4 to about 110% of the stoichiometric, was fluidized at 350° with a current of air at different velocities, *v*. Se was driven off as SeO_2 and As as As_2O_3. *x* of both Se and As increased linearly with log *v*. With *v* sufficient for fluidization, *x* for Se and As was 78 and 72%, resp., whereas at *v* = 0, *x* = 40 and 56%, resp. The max. *x* over 60 min. with *v* = 11 cm. m./kg. granules was 90% Se. 56:2366e C.A.

Recovery of metals which form volatile sulfides from their ores. Metallgesellschaft A.-G. (by Franz Schytil). Ger. 975,020 (Cl. 40a). Appl. Oct. 24, 1951. To recover Sn, Bi, Mo and other metals that form volatile sulfides, ores are treated in a 2-stage furnace in an atm. contg. sulfurizing constituents H_2S, S, and H_2O at 800°. Presence of fine-grained FeS_2 in the solid charge is advantageous. The gravel of the ore is first through a long rotary kiln which discharges into the top of a vortex column furnace where the last stages of the roast take place. The sulfides of Sn, Bi, Mo, Cd, As, etc. enter the gas stream passing through the rotary kiln to a waste-heat boiler and thence to a series of dry and wet electrofilters to ppt. the particles of metal sulfide from the partly cooled gases. 56:2260 O. C. Ralston

The extraction of arsenic from speiss. E. I. Ponomareva, E. G. Svirchevskaya, and L. G. Plekhanov. *Trudy Inst. Met. i Obogashcheniya, Akad. Nauk Kazakh. S.S.R.* 1, 53–7(1959).—Speiss (*a*) contg. Pb 16.3, Cu 35.8, Fe 21.9, SiO_2 0.3, As 18.0, and Sb 0.53% was formed in the lead-smelting furnace in Leninogorsk, southwestern Altai. Sepn. of the speiss compds. by old metallurgical methods was not successful. Extn. of 96.9% As and 84.5% Sb, equiv. to 10% of speiss, was obtained by a new method based on the greater affinity of Cu, Fe, and Pb for S than for As, and the very high volatility of AsS_3 and SbS_3, even at moderate temps. and low pressures. The speiss compds. were sepd. by smelting with pyrite to form a matte low in As, and a new speiss (*b*) enriched with As; the speiss *b* is then resmelted with elemental S. A mixt. of speiss *a* 10 and pyrite 7 parts by wt. was resmelted for 1.5 hrs. at ≤1100° and allowed to settle. The mat contg. the constituents of speiss *a* with recoveries of Pb, Cu, and As equal to 91.3, 60.0, and 0.11% by wt., resp., was by analysis 25.2, 30.5, 0.55%, resp., suitable to ship to the Cu–Pb smelter. The speiss *b* recovered from speiss *a* 2.4, 31.7, and 52.4%, resp., analyzing 1.1, 18.2, and 25.5%, resp., was mixed with free S in a ratio speiss *b*:S of 2:1, and resmelted for 6 hrs. at ≤800°. The total yield of As was 58.2, 91.8, and 96.9% by evapn. for 1, 3, and 6 hrs., resp.; that of Sb, 40.0 and 84.5% after 3 and 6 hrs., resp. Exptl. tests at ≤600° recovered 75% As and 1.8% Sb, in the 3-hr. period of resmelting. Sepn. of As from Sb is achieved by a change of temp. and time of evapn. When the S amts. added to speiss *b* were equiv. to form the sulfides of Cu, Fe, and Pb only, the As evapd. and the Sb remained in speiss *b* as metal. 56:214d Michael J. Ivanoff

Converting polymetallic mat and speiss. O. G. Miller. *Trudy Altaisk. Gorno-Met. Nauch.-Issledovatel Inst., Akad. Nauk Kazakh. S.S.R.* 9, 235–42(1960).—During initial stages of converting, Pb volatilizes from mat as sulfides, and partly as a metal. At later stages the slag is satd. with sulfide vapors. The amt. of volatilized Pb and As does not depend on compn. of blowing gas (O or air), but depends on the form of Pb and As compds. and on the vol. of the blowing gas. The converting of speiss together with mat (both from Pb mills) results in oxidn. of only FeS, whereby the melt becomes enriched in S, which, in turn, decomp. Fe_3As and Cu_3S with the formation of the resp. sulfides and metallic As. The dust contains 2 fractions: coarse, composed of Pb 70 and As 30%, and fine, composed of fine metallic As crystals. The converter slag contains Cu 1.5–4.0, Pb 0.2–5.0, As 0.8–11.0, SiO_2 16–20, Fe 40–8%; it can be returned to production. It is recommended to melt the polymetallic agglomerate with the production of speiss and to process the latter on converters for the production of crude Cu. The fine dust of metallic As should be caught sep. 55:20837i George J. Maleckl

Roasting arsenical pyrites. Bolidens Gruvaktiebolag. Brit. 857,867, Jan. 4, 1961. As_2O_3 is removed from pyrites by roasting them in a fluidized bed at 830–97° while the amt. of SO_2 in the off-take gas is kept within 13.5–15.5%. A sepn. of solids from gas is made at the off-take temp. No reversal of the reaction takes place at >830° or <300°; hence the need to make a sepn. at full temp. and to remove the calcine immediately. Thus, in a typical roast at 900°, the off-take gas contained 15.5% SO_2, and the calcine contained 0.42% S with 0.04–0.05% As_2O_3, which represented 10–13% of the As_2O_3 contained in the feed. 55:13791a Nat L. Shepard

Volatilization of low-boiling elements and compounds during heat treatment. A. A. Babadzhan, V. D. Bulatov, and L. A. Vetrenko. *Byull. Tsvetnoi Met.* 1957, No. 21, 18–20. —The compn. of sublimates obtained by heat treating metallurgical dusts showed that Cu, Fe, Si, and Al passed into the sublimates, due to the entrainment of the processed dust and of air-blown mat. Most sublimation of In and Ge occurred during the first hrs. of the operation. When sulfide concentrates high in In were used, 95% of the In might be removed from the melt, thereby increasing the In content in the sublimates up to 10-fold. Pb, Cd, Tl, and As were more intensively volatilized in the middle of the operation. The Zn content of the sublimates increased as the operation proceeded. From *Referat. Zhur., Met.* 1958, Abstr. No. 11930. 55 : 12208 g — K. L. C.

Beneficiation of arsenic-containing flue dusts. Metallgesellschaft Akt.-Ges. (by Rudolf Michels). Ger. 1,023,583, Jan. 30, 1958 (Cl. 40a). Arsenic-contg. flue dusts from the roasting of pyrite are mixed with fresh pyrite, pelletized with sulfite liquor or H_2SO_4, and roasted at >500°. The Fe content is transformed from Fe_2O_3 and $FeAsO_4$ to Fe_3O_4, and As evaps. The roasted pellets are charged to the roasting furnace. From *C.Z.* 1959, 1055. Kurt Mann

1938

Roasting of arsenopyrite gold-bearing ores. Dorr Co. Brit. 477,050, Aug. 6, 1937. Ore solids are selectively roasted in a fluidizing furnace by passing through the ore an O-bearing gas in a controlled amt. at 450° to a temp. which would fuse the ore particles to produce Fe_2O_3 and volatile As_2O_3 and As sulfide but not nonvolatile As_2O_5. The treated ore is discharged to a 2nd zone in the furnace, maintained in a fluid condition, and oxidized exothermically to a dead roast. H_2O may be used to control the temp. of the roast. Au is recovered by conventional cyaniding. 46 : 11085 W. A. Mudge

Metal distillation and recovery. Anglo American Corp. of South Africa Ltd. Brit. 660,638, Nov. 14, 1951. This invention relates to the vaporization and condensation or oxidation of metals, such as Zn, Cd, As, and Sb, that boil between 400 and 1900°. The process consists of inductively heating and vaporizing the metal, condensing the vapor, feeding fresh metal to the melting cavity at an adjustable rate gravitationally through a liquid-seal trap, and controlling the temp. of the condenser by adjustment of the rate of feeding to the cavity. This process adjusts the cross section of the molten metal in the furnace cavity and thus varies the heat input to the condenser. C. W. Schuck

A safe effective roaster for sulfide ore tests. Oba Wiser (Britannia Mining & Smelting Co. Ltd., Britannia Beach, B.C.). *Eng. Mining J.* 147, No. 7, 65(1946).—An illustrated description in line drawing of a lab.-size roaster for arsenopyrite. Arsenic is recovered as snow-white powder (30–97% As_2O_3). 40 : 5679 g W. H. Boynton

Treatment of refractory arsenical ore at Talgarno. J. C. Watson. *Mining Geol. J.* (Australia) 2, No. 6, 219–22 (1942).—Auriferous arsenopyrite is heated under reducing conditions, As being condensed. The ore is then milled and amalgamated. Recovery of Au is poor and that of As unsatisfactory; dump tailings contain approx. 8% As. Cyanide leaching is recommended; in tests 75–90% of the Au values in the tailings were recovered by a 72-hr. cyanide leach. 36 : 5059 Michael Fleischer

Reclaiming antimony from waste—an economic use for speiss. A. G. Arend. *Chem. Age* (London) 44, 77–8 (1941).—Speiss, a waste product from Ni, Cu and Sn smelting, contains 10–15% Sb which can be recovered. The speiss is first fused with pyrites in a small elec. furnace. This operation seps. as much as 90% of the Cu as matte and the As as a volatile sulfide which can be condensed and the As recovered. The speiss (now chiefly Ni antimonide) is again fused at a dull red heat in a reverberatory furnace with Na_2SO_4 and coal and the mixt. cooled and crushed. Na thioantimonite is dissolved out with boiling H_2O and the Sb recovered by electrolysis in a Fe cell with a c. d. decreasing from 115 to 50 amp. per sq. meter as the liquor strength decreases. The product is powdery and is remelted with a little Sb_2S_3 to free it from most of the Fe picked up. The Sb ingots obtained are 99.9% pure. Cu, Pb and Ni can be recovered from the insol. residue after the leaching. James W. Poynter

Recovery of sulfur and arsenic in the smelting of pyrites. A. R. Lindblad. Swed. 91,402, Feb. 9, 1938. The gases from the shaft furnace in the smelting of pyrites are led together with reducing agents which are being used in the smelting of the pyrites back to the shaft furnace. The quantity of reducing agent is such that practically all the SO_3 and As_2O_3 are reduced; an alkali or alkali compd. is introduced into the furnace to act as catalyst in the process. Examples of reducing agents are generator gas, metallurgical gas, natural gas, gaseous hydrocarbons, petroleum and powdered coal. 32 : 4131 c

Manufacture of carbon disulfide and reduction of arsenic or mercury sulfides. Alfréd Romwalter. Hung. 117,411, Dec. 15, 1937. Ores contg. As or Hg or their sulfides are roasted to produce vapors contg. As and Hg. Horizontal airtight clay or silica retorts are most suitable. The vapors are led through ignited coal. The gases formed are cooled and the CS_2 produced is sepd. from the metallic Hg and As. 32 : 3105 3

Separation of sulfur and arsenic from the ores of Recsk, Hungary. Alfred Romwalter. *Bányász. Kohász. Lapok* 71, 11–12(1938).—Pyrite and enargite from Recsk are first roasted to remove As and a part of S. The As vapors condense in microcryst. As_2O_3 which can be retained by a dust filter. This method is suitable for ores not too high in As. As-rich ores (enargite) or concentrates should be leached with hot KOH or should be dry-distd. In leaching, the reaction is $2Cu_3AsS_4 + 6KOH = 3Cu_2S + K_3AsS_3 + K_3AsO_3S + 3H_2O$. The As compds. thus produced are dried, mixed with lime and roasted to produce Ca arsenate for making plant insecticides. In dry distn. up to 1000° all the As of the ores goes over into the condenser, together with ⅓ of the enargite sulfur and 50% of the pyrite sulfur. On treatment of this mixt. with ammonia As sulfides are dissolved. The undissolved, finely powd. S can be used directly as an add'n. to insecticides. S. S. de F.

32 : 1325 3

Separating arsenious oxide from sulfur-burner gases. S. M. Golyand and B. L. Shneerson. Russ. 41,507, Feb. 28, 1935. To avoid the pptn. of both As and S compds., the gases are preliminarily cooled to about 280–300°, and subjected to elec. pptn., and then passed through a cooler flushed with 30% H_2SO_4 to bring the temp. to 100°, in such a manner as to obtain H_2SO_4 of 62–70%. The gases are then passed through a second set of elec. filters to ppt. the remaining As compds. 30 : 8539 2

Chlorination of Cottrell dust. Ya. Ya. Slobodska. *Trans. Sci. Inst. Fertilizers and Insectofungicides U. S. S. R.* No. 123, 86–104(1935).—The Cottrell dust obtained in Cu foundries contains up to 13% As_2O_3, 15% ZnO and 9.7% PbO. The As is sepd. by an oxidizing, reducing roast (sepn. of As_2O_3) and by chlorination (sepn. of $AsCl_3$). Heating of the dust to incandescence, with access of air, yields 86% of the As_2O_3 at 400°, while in the presence of coal and a temp. of 500°, 92% of the As_2O_3 present in the ore is recovered. $AsCl_3$ is not obtained by chlorination with NaCl, while a yield of up to 83% of $AsCl_3$ can be attained by the use of gaseous Cl at 500°, and the yield can be raised to 99% in the presence of coal and at a temp. of 900°. 30 : 3599 9 A. A. Boehtlingk

Roasting and sintering ores containing sulfur and volatile constituents such as zinc, cadmium, arsenic, etc. Hans Klencke (to American Lurgi Corp.). U. S. 1,984,747, Dec. 18. The pulverulent ore is ignited with fuel such as coke, and the ore, together with excess roasting air, is treated in a layer which retains the solid constituents and contains sufficient incandescent reducing material for reducing and volatilizing volatile constituents. App. is described. 29 : 746 4

Treatment of sulfide ores. Metallges. A.-G. (Hans Klencke, inventor). Ger. 596,619, May 17, 1934 (Cl. 40a. 2.01). Addn. to 563,223 (*C. A.* 27, 937). Pulverulent sulfide ores, with or without another fuel, are ignited in a burner, and the combustion products are filtered through a layer of reducing material, *e. g.*, a mixt. of coke and sintered ore. The conditions are such that oxides of volatile metals in the combustion products are reduced in the filtering layer, the volatile metal vapors then passing through the layer. The process is particularly applicable to sulfide ores of Fe contg. Zn, As and Cd. App. is described. 28: 5030[8]

Alloy. Jesse O. Betterton (to The American Smelting and Refining Co.). Can. 334,295, July 25, 1933. Shot metal is formed by establishing a vortex in a bath of antimonial lead heated to 850–1000°F. A reducing agent as coal, coke or other carbonaceous material together with oxides of arsenic are added to the bath through the vortex. The volatilized As is recovered and collected in a baghouse. 29: 5301[4]

Treatment of antimony, arsenic and mercury ores. Oesterreichische Bamag-Bottner-Werke A.-G. and Rudolf Jahn. Ger. 475,337, Feb. 10, 1926. The powd. ore is passed through a heated rotary tube, preferably of cruciform section, in the same direction as a stream of air, and the oxide fumes so obtained are passed into a separator for solid impurities maintained at such a temp. that the fumes are not condensed. The fumes are then blown into a heated chamber in which they are reduced by powd. C or by gases such as CO or H. The reduction may also be effected by mixing the fumes with the gases and blowing the mixt. through an elec. arc. 23: 3201[6]

Speiss and the metals of the platinum group. H. Rolden and J. Henderson. *J. Chem. Met. and Mining Soc. S. Africa* 29, 65–7(1928).—Fusion speiss is difficult to roast but a finely crushed sample mixed with damp sand (1:1) should be workable in a good roasting furnace with recovery of As. Fusion of the roasted product mixed with mealie meal in a crucible with assay slag as cover is fused 1 hr. at a high temp. and poured into a mold. The resultant bead consists of Ni and Cu with some platinoids. The detached slag is returned to the crucible and given a couple of washes to recover the remaining precious metals in the Pb. This means of collection of the bulk of the Ni and Cu renders their recovery by the usual methods possible. No data are given. 23: 1600[7]

W. H. Boynton

Recovering volatilizable metals from ores. F. Johannsen. U. S. 1,618,204, Feb. 22. Ore contg. Zn, Sn, Pb, Cd, As, Sb, or Bi or a similar material, together with a carbonaceous reducing agent, is continuously charged into a heated metallurgical furnace in which an oxidizing atm. is maintained and travels through the furnace in a layer which is rolled around as it advances. Volatilized metals and combustible gases are burned in contact with the charge and the latter is thus heated to effect reduction and volatilization, without fusion or slagging of the charge in the reduction zone. 21: 1093[4]

Recovery of arsenic and other valuable constituents from speiss. C. P. Lonville. *Trans. Am. Inst. Min. Met. Eng.*, May, 1925 (advance copy) 13 pp.—For the recovery of the constituent metals from a speiss contg. on the av. Pb 21.4, Cu 30.1, Fe 10, Ni 7.3, Co 1.8, As 18.7, Sb 4.6, S 3.4, Zn 2.1% etc., Au 0.76 oz. and Ag 201 oz. per ton, the coarsely crushed material was melted rapidly with 20% of S on a sloping magnesite hearth of an oil-fired reverberatory. The molten product sepd. into 2 layers, a lower layer, 53% of the original speiss, consisting of enriched speiss and an upper layer (65%) of mat. The speiss assayed Pb 4.3, Cu 12, Fe 10, Ni 13, Co 3, As 35, Sb 3.6, S 7%, Ag 37 oz. and Au 1.3 oz. per ton, and the mat, Cu 36, Pb 29, Ni + Co 0.8%, Ag 335 oz. and Au 0.1 oz. per ton. The latter was returned to the blast furnace and the former crushed to pass a 20-mesh sieve, roasted to expel as much As as possible, and fused with 16% of S and sufficient coal to reduce the oxides. The new speiss (26% of original) assayed Pb 2, Cu 10, Fe 7, Ni 25.7, Co 5.9, As 34, Sb 10, S 7%, Au 2.3 oz. and Ag 36 oz. per ton; the mat (10%) contained Pb 17.6, Cu 37.3, Ni and Co 1.8%, Ag 145 oz. and Au 0.7 oz. per ton at the same time 9½% of As was recovered as trioxide in the fume plant. The new speiss was finely ground and again roasted until all the S was expelled, more As being recovered from the fume. The roasted product contained about 16% As and 0.3% S; sufficient Na carbonate was added to combine with all the As and S remaining and roasting was continued in a Godfrey single-hearth furnace until all the As was converted into trisodium arsenate, which was extd. by leaching the material on the counter-current principle, a small quantity of Na_2S being added to the leach liquor after filtering to remove the small quantity of Cu that dissolved. The liquors were evapd. until they solidified on cooling to a product assaying about 56% Na_3AsO_4, 1.3% Na_2SO_4, 1.9% Na_2CO_3, 40% H_2O. The residue from leaching was about 21% of the original speiss and contained Pb 2.5, Cu 12.5, Fe 8.7, As 1.3, Sb 11.7, Ni 31.3, Co 7.4%, Au 2.9 oz. and Ag 46 oz. per ton. This mud was mixed with H_2SO_4 (d. 1.8), passed through a heated rotating drum in a thin stream and into a conical dissolving tank contg. water agitated by a current of air. The overflow from the tank passed to a settling tank. The slimes were thickened by addn. of lime to neutralize acidity and returned to the blast furnace; they contained Pb 5, Sb 25, Cu 3, Co and Ni 2.3%, Au 6 oz. and Ag 97 oz. per ton. The sulfate soln. was electrolyzed for Cu, concd. by steam coils in lead-lined vats to d. 1.45, and finally evapd. in open cast-iron pans to d. 1.65. On cooling the bulk of the metal sulfates sepd. out in the anhyd. form and the supernatant acid was returned to the dissolver. The sulfates were carefully roasted until the Fe and As were rendered insol. and the mass was leached to obtain a soln. of Ni and Co sulfates from which Co was recovered by treatment of the soln. first with limestone to sep. Fe, then with H_2S to remove Cu and Zn, and finally with NaClO to ppt. the Co. 20: 889. B. C. A.

Treating sulfide ores. P. Krupp Akt.-Ges. Grusonwerk. Brit. 234,826, May 30, 1924. Sulfidic ores or similar materials contg. volatilizable metals such as Zn, Pb, Sn, Bi, As and Sb are decomposed, in one operation at a high temp. without previous roasting, to effect volatilization of the metals and combination of the S with the residue. The oxidation of the metallic vapors may then be effected immediately or as a sep. operation. Raw ore is mixed with coke or other reducing material to maintain a strong reducing atm. in the material itself and a neutral atm. adjacent the particles of material so that oxidation of S is avoided. Temps. of 1250–1400° are suitable. Alk. compds. may be added to fix the S; and refractory material such as Al_2O_3, SiO_2 or limestone may be added to prevent liquefaction of the charge. 20: 735.

Fine powders by precipitation from gases. W. K. Lewis. U. S. 1,442,485, Jan. 16. In pptg. fine powders from gases, *e. g.*, ZnO or a sulfide of As or Sb, the gaseous material is highly dild. with combustion gases or other inert gas to facilitate obtainment of the ppted. solid material in very finely divided form. 17: 1096.

Apparatus for recovery of arsenious and selenious oxides. H. Jander. U. S. 1,321,211, Nov. 11. Provision for recovery of As_2O_3 and SeO_2 is made by the association with a pyrites burner of a plurality of cells for condensing the SeO_2 and As_2O_3. Each of the cells is provided with coils to effect cooling and one of them is connected with a reheating device for heating SO_2 in the gases for manuf. of H_2SO_4. 14: 2115.

Separating condensable constituents from gases. W. A. Schmidt and L. Bradley. Brit., 109,106, Sept. 5, 1916. The constituents of a heated gaseous mixt. are sepd. by cooling below the temp. of condensation of one constituent, removing the cloud of condensate in an elec. separator, further cooling to condense a second constituent, and so on. Dust, etc., may be sepd. from the gases in an elec. separator before cooling. The process is applicable for the recovery of As, H_2SO_4, etc., from the flue gases of an ore-roaster. App. is specified. 12: 276.

Plant for treating minerals by volatilization. Soc. des Brevets et Procédés Herrenschmidt. Fr., 481,960, Feb. 6, 1917. In the volatilization of Sb, As, Zn, and Hg minerals, the circulation of the gases of combustion is ensured by aspiration, the major portion of the solid particles being retained in the condensers, while the remainder is collected in H_2O and recovered by decantation. 11: 3231.

Industrial Processes: Removal

84: 94878b Dust removal from gases at high temperatures. Terebenin, A. N.; Bykov, A. P.; Sherstov, V. Ya. (USSR). *Tsvetn. Met.* 1975, (9), 54–5 (Russ). The electrostatic pptn. of elec. furnace dust and fumes was studied at a Sn [7440-31-5] smelter. Increasing the temp. of gas entering the precipitator from 215–25° to 256–88° by decreasing the amt. of cooling spray water decreased the As [7440-38-2] concn. of cleaned gas from 4.7–5.9 to 1.2–2.0%, the moisture content from 178–221 to 150–65 g/m³, the elec. resistance of the dust, the current requirement, and the app. corrosion, and did not affect the 99.1–99.24% gas cleaning efficiency. E. M. Elkin

84: 62041n Extraction of tin from an unconditioned concentrate by a vacuum-thermic method. Isakova, R. A.; Nesterov, V. N.; Tkachenko, O. B.; Nekrasova, T. S.; Volodin, V. N. (USSR). *Miner. Syre* 1975, 25, 73–9 (Russ). A yield of <95% Sn [7440-31-5] was recovered from a conc. contg. 4.7 Sn mainly as cassiterite, As 4.8, Pb 0.7, Zn 0.93, S 11.0, SiO_2 29.3, Al_2O_3 6.3, and CaO 0.52% by sublimation at 800–850° and 0.1 mm Hg for ~30 min in the presence of 20% *pyrite* [1309-36-0]. The highest recovery of Sn was obtained by charging the conc. on the pyrite bed, due to the better utilization of S. More than 99% of the original content of As [7440-38-2] sublimes as well, but As can be sepd. from Sn by fractional condensation. Sn contg. 0.1% As and 3% Pb [7439-92-1] condenses in the high-temp. zone of the condensation system, whereas As sulphides and elementary S contg. <0.1% Sn condense in the cold zone. Only 80% Sn at 1000° and 66% Sn at 800° were recovered when the sublimation was carried out without the addn. of the sulphidizing agent (pyrite). A charge composed of conc. 50, pyrite 10, and coke breeze 40% was used in the pilot plant tests in an app. for continuous sublimation in the pseudo-liq. layer, the addn. of the coke breeze preventing the agglomeration of the charge, and 90.5–95% Sn was recovered, 0.16–0.2% Sn remaining in the residue. L. Kuca

83: 182478f Removal of arsenic from tin-containing powdered industrial products by alkaline electrolysis. Serba, N. G.; Kor'min, Yu. A.; Zhukovskii, V. P.; Davydov, E. V. (Kaz. Politekh. Inst. im. Lenina, Alma-Ata, USSR). *Metall. Obogashch.* 1974, 9, 116–23 (Russ). A process was developed for the alk. electrolysis of a dust contg. Sn [7440-31-5] 26.2, Pb [7439-92-1] 16.9, As [7440-38-2] 6.7, Zn 7.4, S 6.8, and Fe 1.5%, the products of the process being a cake contg. Pb 24, Sn 37.2, As 0.3–0.4, S 0.1–1.0% and an alk. soln. contg. As 94–95 and S 72–96% of their original contents. The dust processed is the sublimate resulting from the treatment of lean Sn concs. by a fuming process. The dust is first subjected to oxidizing roasting at 550° (resulting in the removal of most of the As(III)), then mixed with NaOH soln. (liq./solid ratio = 4, initial NaOH concn. 100 g/dm³), and electrolyzed for 6 hr at 80° at a cathode c.d. 900A/m² and anode c.d. 1500A/m². H. Kucova

83: 167217b Distillation of sulfur, arsenic, tellurium, and bismuth during oxidative roasting of Zodsk gold-containing concentrates. Episkoposyan, M. L.; Bagdasaryan, B. A.; Arutyunyan, A. A.; Galstyan, L. A.; Karibyan, A. N. (USSR). *Nauchn. Soobshch. - Nauchno-Issled. Proektn. Inst. Tsvetn. Metall. "Armniprotsvetmet"* 1973, 3, 55–60 (Russ). The distn. of S [7704-34-9], As [7440-38-2], Te [13494-80-9], and Bi [7440-69-9] was studied during oxidative roasting of Au-Ag concs. for 1–5 hr at 400–900° in a lab. elec. muffle furnace. The curves on distn., as a function of time and temp., showed that the distn. degree of all these elements, except As, increased with temp., with the main part distd. during the 1st 1.5 hr. The max. As distn. was at 400–500°. The rate of As distn. at low temps. (400–500°) was higher than that of S, but at 700–800° S distd. much more rapidly than As. The low degree of As distn. at high temps. was probably caused by As_2O_3 formation, which combined with the charge components to form nonvolatile arsenates. Te evolved at low temps. more rapidly than S but slower than As. The degree of Te distn. was ≤70–2%. At high temps. the rate of Te distn. was always lower than that of S. The degrees of As and S distn. were ≤82 and 97–8%, resp.

83: 150677d Prospects for using vacuum pyroselection of complex-metal raw material. Isakova, R. A. (Inst. Metall. Obogashch., Alma-Ata, USSR). *Vestn. Akad. Nauk Kaz. SSR* 1975, (6), 30–5 (Russ). It is shown by means of supppressed dissocn. and by mass spectrometry that CdS [1306-23-6], ZnS [1314-98-3], HgS [1344-48-5], and Sb_2S_3 [1345-04-6] undergo dissociative evapn. on heating, while PbS [1314-87-0] undergoes mainly congruent evapn. (at 1000° the degree of dissocn. of PbS is approx. 7%). Vacuum evapn. is mainly a surface phenomenon, and the rate of evapn. is inversely related to the square root of the residual pressure and is scarcely affected by the height of the layer and the grain size. Using *pyrite* [1309-36-0], *arsenopyrite* [1303-18-0], *chalcopyrite* [1308-56-1], and *bornite* [1308-82-3] as examples it is shown that in vacuum heating of complex sulfides the temp., residual pressure, and grain size have a significant effect on the rate of decompn. Vacuum heating of Au concs. contg. 3–34% As [7440-38-2] evapn. 98.5–99% of the As in 1 stage. The Au [7440-57-5] can be extd. by well known methods. Vacuum evapn. is also effective in sepg. As from Sn concs. Thus, it can be used to sep. As from a conc. contg. 0.8–3.5% As and 3.7–59.8% Sn [7440-31-5] at 700–750°, which seps. >90% of the As in 1 stage. Extremely good results have been obtained in vacuum evapn. of Au-Sb concs. e.g., a conc. contg. 22.60% Sb [7440-36-0] and 8–20% S, from which 99.5–99% of the Sb could be sepd. and the Au concd. in the residues. In the vacuum evapn. of Cu-Bi and Pb-Bi concs. at 1000–1050° 98–99% of the Bi [7440-69-9] and Pb [7439-92-1] were distd. off, while the Cu [744-05-8] and precious metals could be concd. in the residues. Vacuum evapn. was very effective when combined with oxidn. processes. F. N. Standen

83: 167274t Pilot-plant tests of an absorption method for removing arsenic from gaseous metallurgical sulfur and thermal analysis of products. Isabaev, S. M.; Azimbaev, K. T.; Zhambekov, M. I.; Polukarov, A. N. (USSR). *Tr. Khim.-metallurg. in-ta. AN KazSSR* 1974, (25), 59–63 (Russ). From *Ref. Zh., Metall.* 1975, Abstr. No. 3G337. Title only translated.

72: 114590r Dearsenizing and desulfurizing ferrous ore such as pyrite cinder or the like. Ohkubo, Yasutake; Ogasawara, Shoki; Kitazawa, Tadao (Kowa Seiko Co., Ltd.) Japan. 74 37,603 (Cl. C 21b, C 22b), 11 Oct 1974, Appl. 70 83,800, 26 Sep 1970; 5 pp. Pyrite cinder contg. Fe 57.30, As 0.24, S 0.86, and SiO_2 13.7% is mixed with 1.5–4.0% coal or coke, ground, and agglomerated to grains contg. 41% of −44μ. The powder is moistened with ~12% water and pelletized to 10–15 mm diam. The pellets are calcined at 950–1150° in a rotary kiln with a neutral or oxidizing atm. The removal of As and S has an efficiency of >90%.

77: 33702b Removal of impurities from molten copper sulfide by gas injection. Shima, Masao; Nakao, Sei (Furukawa Mining Co., Ltd.) Japan. Kokai 74 94,518 (Cl. 10 L121 D), 07 Sep 1974, Appl. 73 6425, 12 Jan 1973; 3 pp. N_2, CO, CO_2, and/or SO_2 gas is injected into molten Cu sulfide, intermediate product in the refining of Cu sulfide ore, to remove impurities such as Pb, Zn, As, Bi, and Sb from the molten Cu sulfide. Thus, N_2 gas was injected into molten Cu sulfide contg. Cu 44.5, Pb 2.12, Zn 5.42, As 0.67, Sb 0.18, and Bi 0.10% at 1.0 m³/hr ton for 4 hr. The resulting molten Cu sulfide contained Cu 50.2, Pb 0.21, Zn 1.65, As 0.10, Sb 0.11, and Bi 0.011%.

77: 33551u Purification of selenium dioxide. Schering, Johann; Lampert, Ingolf (Siemens A.-G.) Ger. Offen. 2,263,197 (Cl. C 01b), 27 Jun 1974, Appl. P 22 63 407.7, 21 Dec 1972; 6 pp. SeO_2 is purified by passing it with N carrier gas through a heated sepg. column, filled with alkali-contg. ceramic spheres as adsorbent for As_2O_3 at inlet and outlet temps. 450 and 320°, resp., and condensation in a receiver at <316°. This procedure was applied to the purifn. of Se by oxidn., distn., and redn.

81: 124611e Reprocessing of fine-grained concentrates. Strizhov, G. F.; Myasnikov, P. A.; Okunev, A. I.; Parinov, V. A.; Golubov, V. P.; Tkachenko, Yu. D.; Sukhankin, V. P.; Chistopolov, V. A.; Ilin, A. N.; et al. (All-Union Scientific Research Institute of Metllurgical ThermalEngineering; "Umlenergotsvetmet" Industrial-Technical Association; Ural Institute of Metallurgy; Ryazan Plant for Preparation and Processing Nonferrous Metals) U.S.S.R. 420,687 (Cl. C 22b), 25 Mar 1974, Appl. 1,774,981, Appl. 20 Apr 1972. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1974, 51(11), 98. Reprocessing of fine-grained concns., such as As-contg. Sn sulfide concs., included a 2-stage roasting. To increase both the efficiency and the removal of impurities, the initial charge was divided into 2 parts; one of which was supplied continuously into the 1st stage of roasting, while the remaining part was supplied into the 2nd stage of roasting. The hot cinders from the 2nd stage (with the degree of desulfurizing and dearsenizing 40–70%) was supplied continuously into the charge layer at the 1st stage of roasting, and then both parts of charge were mixed together for further roasting.

81: 66956y Roasting sulfide ores to remove arsenic in high-moisture content atmosphere. Ohkubo, Yasutake; Ogasawara, Masami; Kitazawa, Tadao (Kowa Seiko Co., Ltd.) Japan. 73 40,162 (Cl. C 22b, C 21b), 29 Nov 1973, Appl. 68 91,560, 16 Dec 1968; 7 pp. Arsenic is removed from the mixed sulfide ore of As-bearing roasted ore and sulfide conc. by roasting in a fluidized furnace at 900–1050° in an atm. contg. 15–30% moisture. Thus, a mixt. contg. 1 part of the roasted ore (55.85% Fe and 0.305% As) and 6 parts of the sulfide conc. (32.25% Fe, 48.20% S, and 0.09% As) having a water content of 25% was roasted in a fluidized furnace at 970°. The degree of As removal was improved to 79.3% by increasing the moisture content in the atm. contg. SO_2 12.25, N 64.32, and O 1.58–21.85%.

81: 47131a Roasting coarse-grained crude arsenical pyrite in three steps, with production of hematitic dearsenified ashes. Rodriguez Duran, Felipe (Fosfonco Espanol, S. A.) Span. 419,451 (Cl. C 21b), 16 Jan 1974, Appl. 419,451, 05 Oct 1973; 17 pp. Roasting of pyrites high in As in fluidized bed furnaces yields a hematitic product contg. magnetite and ≤0.07% As in a 3-step process that involves heating coarse-grained ore with air maintaining a 1% excess of free O for the entire process: (1) at ~850°, (2) the resulting coarser product in 2nd furnace at ~920°, and (3) the intermediate-sized product recovered from the cyclones at 520° in a 3rd furnace. The effluent gases contain no free S. The preferred particle size of the feed is 70% of >1 mm diam. and 35% of ≥3.5 mm diam.
H. A. Goldsmith

81: 28100d Recovery of mercury from copper sulfide ore by selective oxidation. Marshall, James Edward F. (Gortdrum Mines (Ireland) Ltd.) Brit. 1,319,507 (Cl. C 22b), 03 Apr 1974, Appl. 48,297/69, 01 Apr 1970; 3 pp. Hg is recovered from tennantite-tetrahedrite and cinnabar ore conc. before Cu smelting by heating the ore 100–20 min at 450–500° in atm. contg. ≤5 vol. % O to distil Hg free of As and Sb. Subsequent heating to ≥800° distils As and Sb oxides. Alternatively heating to ≤800° in a reducing atm. distils As and Sb sulfides.

80: 111131q Behavior of arsenic during the sintering of Kerch ores. Kuleev, B. K.; Kuleshov, R. N. (USSR). *Obogashch. Rud* 1973, 18(4), 10–14 (Russ). The sintering of Kerch Fe ores rich in As (0.12–0.14%) was studied. The As in the ore is bound to acid-sol. minerals and silicate compds. The addn. of limestone to the charge decreases the volatilization of As from 25% to 15.9–13.7% with the ores and to 18.7% with the washed conc. The addn. of chlorides increases the volatilization of As but also deteriorates the sinter quality. The best results in removing As were obtained either by using a combination heating at ~1100° with town gas, or by the addn. of Fe-flux into the charge, which increases the As removal to 27–30%, improves the quality of the sinter, and increases the productivity. The Fe-flux was obtained from a washed Kerch conc. having a basicity of 5.
V. Dundr

80: 6607b Purification of roasting gas containing arsenic compounds. Ojima, Masao (Ebara Manufg Co., Ltd.) Japan. Kokai 73 00,193 (Cl. 15 B112, 15 B7, 13(7)A11), 05 Jan 1973, Appl. 71 34,947, 22 May 1971; 3 pp. A roasting gas is introduced to a purifying column, contacted with a circulated acid, cooled to a temp. below the solidifying temp. of As oxide vapor, and simultaneously SO_3 in the roasting gas is converted to H_2SO_4. A major portion of the As oxide ppt. is removed from the waste H_2SO_4 in a crude separator. The H_2SO_4 contg. the residual As oxide ppt. is dild. from a concn. in the neighborhood of the min. 1st peak of the soly. of the As oxide to a concn. corresponding to the high soly. of the As oxide. The unsatd. As oxide is recycled. The sepn. of As oxide ppt. from the waste acid is fast, and consequently the treatment of the roasting gas is also fast. The process can be applied to H_2SO_4 manuf. and steelmaking.

80: 62425c Low-impurity iron ore pellets. Ohkubo, Yasutake; Ogasawara, Masami; Kitazawa, Tadao (Kowa Seiko Co., Ltd.) Japan. 73 29,441 (Cl. C 22b, C 21b), 10 Sep 1973, Appl. 69 18,589, 13 Mar 1969; 3 pp. A process for making metallurgical pellets of low impurity content comprises the steps of As removal by roasting at 950 ± 40° the pellets of As-, Cu-, and Pb-contg. roasted sulfide ores or powdered Fe ores added with reducing agents, immersing the roasted pellets in a $CaCl_2$ soln., and chloridizing roasting to volatilize the impurities in a rotary kiln at 950–1250°. Thus, a roasted ore contg. Fe 60.50, As 0.275, Cu 0.603, and Pb 0.252% was mixed with 4.5% coke, pelletized to 10–20 mm. then roasted at 950° for 20 min to remove 91% of the As. The roasted pellets were immersed in a 25% $CaCl_2$ soln. for 5 min, dried at 200°, then roasted in a rotary kiln at 1250° to remove 87 and 93% of the Cu and Pb resp. The resulting pellets had a compaction strength of 405 kg/pellet.

80: 50862e Treatment of noble metal-containing lead sludge. Tamura, Kunihiko; Odajima, Eiko; Kawakita, Shizuo (Mitsubishi Metal Mining Co., Ltd.) Japan. 73 26,573 (Cl. C 22b), 13 Aug 1973, Appl. 68 50,542, 19 Jul 1968; 2 pp. Pb sludge from electrolytic cells is treated to remove impurities and recover noble metals, such as Ag and Au. The treatment efficiency is improved by melting the sludge in a rotary furnace at >1000° and blowing compressed air into the melt from a lance at an angle of 70–90° to the melt surface. Thus, after charging 551 kg Pb sludge contg. Au + Ag 18.05, As + Sb 30.48, Pb 20.05, and Bi 26.31% into a rotary furnace at 1150°, 6 kg/cm² compressed air was blown at 3 m³/min. Sb and As were 1st evaporated and after 40 hr, no As vapor was detected. Then, 2014 kg Pb sludge was charged and the PbO was removed. Then, 764 kg addnl. Pb sludge was added, As and Sb evaporated and 1575 kg refined product contg. Ag + Au 93.01, As + Sb 0.52, Pb 2.15, and Bi 3.01% was obtained.

80: 29420z Vacuum refining technique for removal of impurities from copper. Komorova, Ludmila (Vys. Sk. Tech., Kosice, Czech.). *Hutn. Listy* 1973, 28(8), 577–82 (Czech). Refining raw Cu in a vacuum at 1200° effectively removed impurities Zn 75.8, Pb 63.7, Bi 66.2, As 66.5, and Sb 62.0% of that originally present. The mechanism involved their removal as metal vapors or volatile oxides. Removal of Sn was only 35.0%.
R. C. Chudacek

80 5923q Fluidized roasting of complex pyrites (tunnel furnace). III. Actual operating conditions. Vian, A.; Municio, V. M.; Iriarte, C.; Romero, A. (Div. Invest. Desarrollo Ind., Auxini, S. A., Madrid, Spain). *Ion (Madrid)* 1973, 33(382), 235–41 (Span). Ideal conditions for volatilization of sulfides of As, Sb, and Pb with retention of Cu and Zn sulfides in the fluidized-bed roasting of crushed pyrites in a tunnel furnace are expressed by the relation $U = \delta E/300D_p$, in which δE is the residence time in sec for transit of the ore through the tunnel furnace and D_p is the particle size in mm of the granulated pyrites. Detn. of these parameters and their use under specific working conditions are described. C. R. Addinall

[illegible]:149117t Behavior of nonferrous metals during ferromolybdenum production. Lastovitskaya, K. S.; Zaiko, V. P.; Leitsin, V. A.; Kalinskii, Ya. M.; Fedorenko, Z. M. (USSR). *Sb. Tr., Chelyabinsk. Elektromet. Komb.* 1972, No. 3, 131–5 (Russ). From Ref. Zh., Met. 1972, Abstr. No. 10V252. During Mo-conc. roasting, >90 Se, 50–60 Re, and 30–40% As were converted to gas phase. Pb content was reduced by a factor of 1.5–2. Cu, Sn, and Re became metallic, and 80–90 Bi and Pb was vaporized during the metallothermic process.

79:83056e Removal of arsenic trioxide from roasting gases. Terebenin, A. N.; Bykov, A. P. (Central Scientific-Research Institute of the Tin Industry) U.S.S.R. 380,335 (Cl. B 01d), 15 May 1973, Appl. 08 Jul 1971. From *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* 1973, 50(21), 21. As_2O_3 was sepd. by its condensation during cooling of the gas stream. To obtain the As_2O_3 deposit in the form of coarse aerosol particles, the gas stream (after reaching the dew-point) was cooled maintaining the difference 4–12° between the temp. of central part of the stream and the condensation surface. The gas stream supplied into the condensation zone was cooled at a rate 2–5°/cm.

[illegible]:56239z Roasting of copper-pyrite concentrate in neutral and reducing media. Karoleva, V.; Vasilev, Khr.; Stoitseva, R. (Bulg.). *God. Vissh. Khimikotekhnol. Inst., Sofia* 1969 (Pub. 1971). 16(1), 121–39 (Bulg). Roasting of dried concs. [contg. Cu mainly as chalcopyrite) 3.15, Zn 0.2, Pb 0.16, As 1.22, Sb 0.11, e 31.56, S 38.87, SiO_2 16.1, Al_2O_3 6.7, CaO 0.49, MgO 0.18% and mall amts. of Se, Te, Tl, Ge, Au, and Ag) in N for 1 hr. at 700–900° removed ~ 90% of the As and Sb, 40% of the S, and most of the Te, Se, and Ge; such roasting decompd. most sulfide inerals in the conc., rounded the edges of the grains, and aused agglomeration of the residual sulfides. Roasting in CO aused similar changes, but in this case, it occurred at lower temps., i.e., 500–600°.
T. Ordentlich

79:56261j High-temperature smelting of gold-containing oncentrates. Grigor'yan, G. B. (USSR). *Prom. Arm.* 1972, 10), 40–1 (Russ). The smelting of a Au-contg. conc. from the odsk deposit (Au 58, Ag 87 g/ton, Cu 0.63, S 24.32, Fe 25.72, As 8.7, Pb 0.48, Zn 0.72, Te 0.0016, Bi 0.019, Sb 0.2, SiO_2 17.44, Al_2O_3 8.52, CaO 1.05, and MgO 10.65 wt. %) at 1400–1500° in a educing atm. produced by mixing fine graphite with the charge ith addn. of 9–17 wt. % CaO or soda resulted in formation of an e melt (Fe 75.7, As 2.08, Cu 2.30 wt. %, Au 210, and Ag 300 g/ton), and a slag (SiO_2 32.35, Al_2O_3 9.2, MgO 21.18, CaO 20.6, Fe 10.72, As 0.16, Cu 0.077 wt. %, Au 1.2, and Ag 0.3 g/ton). he extns. of Au and Ag into the Fe melt were 93.7 and 99.7 wt. , resp., also Cu 97, Fe 90, and As 7 wt. %. The yields of Fe melt and slag were 24 and 52 wt. % of the charge, resp. The extns. of As and S into the gas phase were 92 and 35%, resp., as well as Bi + Te 60–80 and Sb 90 wt. %. The optimal CaO addn. nge was 6–15 wt. % of the charge and of Na_2CO_3 10 wt.%.

79:9257n Improvement of electrofiltrational removal of a sulfuric acid fog from a gas. Goncharov, A. E.; Fedotov, M. V. (USSR). *Khim. Prom. (Moscow)* 1973, 49(4), 289–91 (Russ). H_2SO_4 fog, dust, As and Te oxides are removed from SO_2 either in pyrite-based contact H_2SO_4 manuf. or in effluent gases of nonferrous metallurgy by a 4-stage one-sectional, wet, ShMK-type elec. filter. The cylindrical steel body of these filters is laminated with polyisobutylene or covered with acid-resistant brick. The electrodes consist of hexagonal Pb pipes; a lead-deposited star-shaped steel filament is the corona electrode. Two-stage elec. trapping may assure the desired gas purifn. from hazardous admixtures: H_2SO_4 fog ≤5 mg/m³, As —0.005 mg/m³, dust and Se completely trapped. The combined use of evaporating conditions in gas-washing towers and of corona filaments in wet elec. filters allows a decrease in capital losses and in time of erection of new washing depts.
E. Strossberg

78:76388p Macrokinetics of pyrite dearsenization in inert medium. Calistru, C.; Mihaila, Gh. ("Al. I. Cuza" Univ., Iasi, Rom.). *An. Stiint. Univ. "Al. I. Cuza" Iasi, Sect. Ic* 1972, 18(2), 113–21 (Eng). The macrokinetics of pyrite dearsenization was studied at 500–40° by using a pyrite with an initial As content of 1.24%. For a dearsenization degree of <—0.6, the process can be described by a macrokinetic model of transformation while for a dearsenization degree >0.6, the process follows a macrokinetic model of As diffusion through layer of FeS. The As transfer through the external gaseous phase is established as not being the rate-controlling step of the process

77:78134f Purification of copper sulfide ores. Shima, Mashao; Nakao, Sei; Ashio, Kamitsuga (Furukawa Mining Co., Ltd.) Ger. Offen. 2,162,077 (Cl. C 22b), 22 Jun 1972, Japan. Appl. 70 112,044, 15 Dec 1970; 13 pp. Pb, Zn, As, Sb, and Bi were removed from Cu sulfide ores in a 1-stage process by melting in vacuo (10–0.2 mm) and sublimation. Thus, 275 g Cu sulfide ore regulus contg. Cu 48.73, Fe 20.32, As 0.58, Sb 0.19, Bi 0.040, Pb 0.11, and Zn 4.27% was melted at 1230° and treated 1 hr in vacuo (0.5–0.2 mm) with occasional stirring to give a product contg. Cu 52.22, Fe 21.88, As 0.08, Sb 0.04, Bi 0.006, Pb 0, and Zn 0.05%.

77:64956p Behavior of copper, zinc, and arsenic sulfides during the roasting of iron pyrites. Kolta, G. A.; Askar, M. H. (Natl. Res. Cent., Cairo, UAR). *U.A.R. J. Chem.* 1971, 14(4), 73–83 (Eng). A Turkish pyrite conc. (Fe 42.4, S 52, SiO_2 2.8, Cu 0.56, Zn 1.97, and As 0.05%) was roasted in static and fluidized beds at 500–800° in O-N gas mixts. In static beds at 600°, 80% of the As was sublimed as As sulfide and oxide; at 700° ~ 92% of the Zn was transformed to oxide and Cu was present only as oxide. In fluidized beds, the conversion to CuSO, and ZnSO, was influenced by the change of temp., gas compn., gas velocity, and particle size. Not more than 70% of As could be eliminated in 1-step fluidization roasting at 600° when the fluidizing gas contained 5% O. In a 2-step fluidization roasting process the As was completely removed and the concns. of $CuSO_4$ and $ZnSO_4$ were lower than in the 1-step process.
M. A. El-Tarabolsi

77:37159z Dearsenication of phosphate rock. Smith, Raymond Anthony; Sansom, John N. (Electric Reduction Co. of Canada, Ltd.) U.S. 3,652,210 (Cl. 23/165; C 01b), 28 Mar 1972, Brit. Appl. 33,065/68, 11 Jul 1968; 5 pp. Ground phosphate rock is mixed with sufficient H_3PO_4 to bring the $CaO:P_2O_5$ ratio to <3:1 and the mixt. is allowed to dry. The dry material is ground and calcined at 1200–300° in the presence of H_2O vapor. As being volatilized. Thus, phosphate rock contg. 21 ppm As was treated to prep. a calcine contg. 0.2 ppm As. Such products are useful for prepg. food-grade H_3PO_4 by an electrothermal process.
E. C. Houston

[illegible] 143755o Eliminating arsenic from arseniferous nickel ores. Coheur, Pierre Belg. 766,687 21 Oct 1971, Appl. 21 Apr 1971. 9 pp. The As in Ni ores such as laterites is removed during the roasting process by using a reducing flame at ≥1200°. The ore is mixed with 1–5% of a solid fuel and (or) an alk. material such as $CaCO_3$ to diminish the acidity of the gangue in the ore.
Friedrich Epstein

76:117182w Purification of industrial gases containing a large amount of arsenic. Yur'ev, N. V.; Noskov, V. D.; Komarov, E. V.; Polunin, I. P. (USSR). *Tsvet. Metal.* 1972, 45(2), 28–30 (Russ). Purification tests are given of gas from a roaster contg. As ~5 g/m³ using a dry Cottrell precipitator, a packed scrubber, and a wet Cottrell precipitator, all in series. The scrubber soln. was used to wash the precipitators, and sent periodically to ppt. the As_2O_3 with $Ca(OH)_2$. The design and performance are given of the packed scrubber, a turbulent high-velocity Venturi scrubber, and Cottrell precipitator. Tests showed that a packed scrubber followed by a wet Cottrell precipitator gave high purification efficiency. The turbulent scrubber was less efficient than the Cottrell precipitator, but was useful at high loading of insol. dust, when a high degree of purification was not required, and where the gas vol. was small.
E. M. Elkin

[illegible] 88590t Removal of arsenic from the [iron] ores of Kerch [USSR]. Dumitru, Lucia; Nadu, Florica; Mitu, A.; Nicolae, P.; Tripsa, I. (Inst. Cercet. Metal., Bucharest, Rom.). *Cercet. Met., Inst. Cercet. Met., Bucharest* 1971, 12, 51–60 (Rom). Lab. and pilot plant expts. of dearsenization at 1000° were made on Kerch ores from Russia. The chem. compn. of the ore was: Fe 43.97, SiO_2 14.44, Al_2O_3 4.85, CaO 1.51, MgO 1.32, As 0.10, S 0.035, and MnO 1.61%. After processing the ores in a rotary furnace a sintered granular material with a low-As content was obtained. The compn. of this sinter was: Fe 51.35, FeO 18.76, Fe_2O_3 15.63, CaO 0.69, Al_2O_3 5.90, MgO 1.05, Mn 1.33, P 1.29, S 0.004, and As 0.0039%.
G. T. Motock

[illegible] 88570m Removal of arsenic from copper-tin sulfide concentrates by heat treatment. Murkin, V. A.; Beloglazov, K. K. (USSR). *Tr. Proekt. Nauch.-Issled. Inst. "Gipronikel"* (Gos. *Inst. Proekt. Predpr. Nikelevoi Prom.*) 1971, No. 51, 38–51 (Russ). The removal of As from Cu-Sn conc. of the Festival'noe ore (Far East), contg. $CuFeS_2$ 35–43, SnO_2 0.4–1.2, $FeAsS$ 3.5–13.5, ZnS 4–4.5, PbS 0.4–0.8, FeS_2 11–12, Bu_2S_3 0.2–0.3, and gang minerals 16–40% was considered by thermal treatment in Ar, CO, CO_2, and CO + CO_2 atms. at 650–850° for 10–45 min. The compn. of the gas phase affected noticeably Sn distribution. Increase in CO concn. in a gas mixt. >20% increased Sn loss in comparison with thermal treatment in Ar atm. Therefore, the CO + CO_2 gas mixts., contg. <20% CO, which correspond to the combustion of fuel with air excess coeff. 0.9–1, are most favorable for distg. out As with preservation of max. Sn in the cake. During this type of thermal treatment, the Sn loss was ≤2%, and sublimates consisted mostly of elemental S and As sulfide.

72:69582v Roasting sulfurous ores. Societe Anon. Heurtey Fr. 1,572,211 (Cl. C 21b, C 22b), 27 Jun 1969, Appl. 15 Jan 68; 8 pp. In a process for roasting sulfurous ores, esp. As-contg. pyrites, the As-contg. ashes formed in the roasting step in mech. agitated furnaces are mixed and transported together with the powd. or granulated ore (pyrite) and are passed into an evacuation chamber, where the ashes are entrained by the gas and smoke of the roasting furnace and carried away to a zone of the furnace where they are subjected to an addnl. heating step to remove the As_2O_3, and to improve the degree of desulfurization. Equipment conducting the process is described.
Friedrich Epstein

[illegible] 5349s Roasting pyrite. Boliden Atkiebolag Fr. Addn. 93,221 (Cl. C 21b), 28 Feb 1969, Swed. Appl. 21 Mar 1967; 2 pp. Addn. to Fr. 1,463,971 (see Belg. 671,902, *CA* 65: 8432h). The gases from the roaster (BASF-type fluidized bed) with low partial pressure pass through cyclones to sep. the magnetite, then through a recovery unit and an electrostatic filter. Oxidizing gas, to effect combustion of S to SO_2, is introduced after the heat recovery unit, in which the temp. of the gases is lowered from 700–1100° to <420°, but not so far as to cause pptn. of S. With earlier introduction, Fe oxides are liable to be converted to sulfate, ppt. on the tubes of the unit, and interfere with their heat transfer. As_2O_3 passes as gas through the electrostatic filter and is largely recovered as solid in the washings.

71: 52782s Behavior of nonferrous metal impurities in nickel and iron during their in vacuo melting. Chernov, B. G.; Ageev, P. Ya. (Leningrad. Politekh. Inst., Leningrad, USSR). *Stal'* 1969, 29(6), 521 (Russ). A total of 0.05–0.1% As, Sb, Sn, Bi and Pb were introduced without breaking the vacuum in molten Fe and Ni under 0.5 and 10^{-3} torr and held for up to 100 min. No Sn, Sb, or As volatilized from Ni; Pb and Bi loss was proportional to the time and lower vacuum. Molten Fe holds As and Sn; Bi, Pb, and Sb volatilize as a function of lower vacuum and longer holding time.
John D. Gat

69: 21286n Dearsenification of pyrite. Moldovan, Iuliu; Preda, Nicolae; Cruder, Galina M. (Romania, Ministry of the Chemical Industry) Rom. 49,473 (Cl. C 21b), 04 Dec 1967, Appl. 04 Jun 1966; 2 pp. To reduce the As content below the required limit for iron metallurgy, the pyrite, intended for oxidizing roasting in a fluidized bed, was previously roasted at 500–600° in a mixt. of air in substoichiometric amt. and reducing or inert gas. The latter was added in an amt. corresponding to the required pressure, either for carrying along As_2O_3 and SO_2 obtained by burning labile S of pyrite in an app. for recovering As_2O_3, or for the pneumatic transport of the pyrite to the fluidized-bed furnace. Thus, a pyrite contg. 0.6% As, ground to a size suitable for the fluidized bed, was roasted with 100 m.³ air/hr. for every 100 kg. pyrite. The introduction of reducing or inert gas or recycled SO_2 was adjusted in such a manner that the pressure loss was ≤120 mm. water. Under these conditions, the As content of the preroasted pyrite was <0.045% and the ash of the fluidization furnace had <0.05% As. SO_2 for manufg. H_2SO_4 was free of As oxides. Conventional equipment with very few modifications could be used.
Marcel M. Gregorian

68: 5169a Extraction of arsenic from technological dust from tin production. S. A. Alekseev, L. E. Bulgakova, R. V. Turgumbaeva, G. N. Zimina, and I. I. Andreev. U.S.S.R. 190,024 (Cl. C 22b), Dec. 16, 1966, Appl. Nov. 16, 1964. Arsenic is extd. by soda with preliminary removal of S and Cl. To increase the extn. of As and decrease the consumption of the reagents, the dust is mixed with a soda pulp, dried, and then roasted at 500–600° for 2–4 hrs. in an oxidizing atm., which ensures the conversion of the As into H_2O-sol. Na_3AsO_4. From *Izobret., Prom. Obraztsy, Tovarnye Znaki* 44(1), 74(1967).
MHCL

Behavior of sulfur in the sublimation of arsenic from copper arsenide. G. N. Zviadadze and L. S. Tabatadze. *Tr., Gruzinsk. Inst. Met.* 14, 281–2(1965)(Russ). The behavior of S during sublimation of As obtained by thermal dissocn. of FeAsS from the Tsan deposit in a mixt. with Cu_3As was studied. The As contained 0.04% S. After sublimation of As, the S content was 0.0008%. No Cu contamination was detected. Bi and Sb contents were also considerably reduced. From *Ref. Zh., Met., G.* 1966, Abstr. No. 2G173.
MVTK

Sublimation of nonferrous metal impurities. Metallgesellschaft A.-G. (by Karl Lippert). Ger. 1,213,122 (Cl. C 22b), March 24, 1966, Appl. Jan. 12, 1965; 2 pp. As, Sb, Zn, etc. are removed from oxide ores by subliming them in the form of chlorides. Roaster dust and other material to be purified is pelletized with a $CaCl_2$ soln. or slurry and heated at 1000° in a reducing atm. If a great deal of Zn is to be removed, the water content of the reforming gas must be kept low. Thus, a flue dust was pelletized with a $CaCl_2$ aq. soln. contg. 250 g./l., and after drying the pellets contained Cu 0.13, Zn 0.23, Pb 3.1, As 0.45, Sb 0.23, Sn 0.04, S 1.29, and Cl 2.8% by wt. The pellets were heated in a furnace at 1000° in a stream of gas contg. H 5, H_2O 25, and N 70% by vol. The residue after 90 min. heating contained Cu 0.10, Zn 0.20, Pb 0.05, Sn 0.012, As 0.023, Sb 0.022, S 0.25, and Cl 0.07% by wt. A mixt contg 1.18% Zn was treated with a gas contg. CO 10, CO_2 20, H_2O 2, and N 68% by vol.
64: 15452b T. A. Ratkay

Extraction of lead and zinc from concentrates by sublimation in vacuum. R. A. Isakova, V. S. Esyutin, and V. N. Nesterov. *Kompleksn. Pererabotka Polimetal. Syr'ya, Kazakhsk. Politekhn. Inst., Tr. Vses. Nauchn.-Techn. Konf.* 1962, 215–21(Pub. 1965) (Russ). The vaporization of sulfides in vacuum depends on the element forming the sulfide: either the sulfides pass directly into the vapor from the solid phase (As, Ge, Sb, Ta, Sn, Pb, Cd, and Bi) or they have to be heated to the softening or m.p. with increase in vacuum (Ca, In, and Zn), or they cannot be vaporized by increasing temp. and by the length of vacuum treatment since their dissocn. pressure is higher than their vapor pressure. The vacuum processing of the complex products produces the extn. of volatile components by sublimation, and by fractional condensation of vapors, a selective sepn. of sulfides. The condensation temps. for ZnS, PbS, Sb_2S_3, and As_2S_3 are 750–600, 550–500, 500–00, and 280–200°, resp. The complicated app. is the main disadvantage of the vacuum processing, but in many instances it is very useful, since it eliminates an entire process, e.g. vacuum eatment of the matte increases Cu content to such an extent at the concn. of the matte by fusion is eliminated. 64:4765f

Extraction of zinc and lead from complex matte by evaporation in vacuum. R. A. Isakova, V. N. Nesterov, and A. L. Tseft. *Tr. Inst. Met. i Obogashch., Akad. Nauk Kaz. SSR* 8, 13–18 (1963). Expts. were made in a lab. app. described previously. Also, an enlarged lab. (small pilot plant) was built and is described. The effects were studied of final pressure, temp., thickness of the layer of Pb–Zn melt, length of vacuum application, and distribution of rare, and disseminated metals. Optimum vacuum level at 1200° was 0.1–1 mm., at which the extn. of Pb or Zn was ~99%; the matte layer should be ≤40 mm. thick. Evapn. degree at 900, 1000, 1100, and 1200° for Zn was 43.0, 37, 99.2, and 99.6%, resp., while for Pb it was 90.3, 72.0, 99.9, and 99.6% resp. The initial matte contained Zn 10.25 and Pb 15.45%. The higher evapn. degree at 900° than at 1000° was attributed to larger surface of evapn. when the matte was still solid (at 900°). The duration of vacuum application had no effect at 15–180 min. At 1100–1200° and 0.1–1.0 mm., In, As, Sb, and Cd evapd. completely into the gas phase, while Ga was distributed evenly between the residue and the condensate. Of importance is the fact that Cu is considerably enriched in the residue (from 17.05 to 26.2% after 30 min.) so that concentration smelting of poor matte may not be necessary. Optimum conditions were 1200°, 30 min., and 0.1 mm., when the degrees of evapn. of Zn and Pb were 96 and 99% resp. 60:15485c GMJR

Investigations concerning the metallurgical treatment of pyrrhotite containing cobalt. Sulfatizing roasting of the ore freed from arsenic. Yasuaki Ueda. *Nippon Kogyo Kaishi* 80, 29–33(1964)(Japan); cf. *CA* 58, 13493d. In the prepn. of $FeAsS$ contg. Co at >700° in a vacuum, the As is volatilized >93% as As and As_2S_3. The most effective roasting temp. for the pyrrhotite residue which contains the Co and for the conversion of Co into sol. form is 550–75°. From the roasted ore >70% Co can be leached out with H_2O and ~90% Co with 10% H_2SO_4. From *CZ* 1964(45), Abstr. No. 2075. MCCR

Purification of tin by vacuum distillation. N. N. Murach and L. G. Povedskaya. *Sb. Nauchn. Tr., Inst. Tsvetn. Metal.* No. 35, 56–67(1963). The purification of Sn by the volatilization at 900–1000° of As, Sb, Bi, and Pb impurities under vacuum (10^{-1} to 10^{-3} mm.) was studied for each of the binary Sn-contg. systems and for "black tin" contg. 0.49% Pb, 0.018% Bi, 1.22% As, and 0.078% Sb. In Pb–Sn systems contg. 1–5% Pb, the Pb is completely removed in 1 hr. at 1000° and 10^{-1} mm. For Bi–Sn systems contg. 0.32–0.6% Bi, the Bi removal is 99.4–100.0% complete under similar conditions. In Sn–As systems (0.9% As) it was difficult to reduce the As level below 0.2% at 1000°, despite the relatively high vapor pressure of pure As. To remove As completely it is necessary to go to 1100°, at which temp. the loss of the As is accompanied by a 5% loss in Sn. Sb losses for Sn–Sb systems (contg. 0.17–0.29% Sb) amounted to only 56.5% after 2 hrs. at 1000° and 10^{-1} mm.; and 62.4% after 1 hr. at 900° and 10^{-1} mm. Black tin could be purified in large-scale (200-g.) expts. at 950–1000° and 10^{-1} mm. for 1–3 hrs., so that virtually all the Pb and Bi, 80.8–99.5% of the As, and 58.7–80.8% of the Sb were removed. 60:3217d C. H. Fuchsman

Sintering fine iron ores containing arsenic. Arthur M. Schwarz (to Inland Steel Co.). U.S. 3,166,403 (Cl. 75–5), Jan. 19, 1965, Appl. Feb 24, 1960; 8 pp. In the sintering of fine Fe ore contg. As in conventional Dwight-Lloyd machines to prep. the ore for blast-furnace smelting, the As is largely eliminated from the sinter and recovered from flue gas, without losing the advantages of incorporating lime in the sinter for fluxing, by operating the sintering machine with 2 layers of fine ore and coke, topd. by a nonsintering layer of limestone, the bottom layer being sintered without lime or other flux so that the heating drives off the As, and being collected sep. from the top layer and recycled As-free to the charge for the top layer, which can then be made self-fluxing and collected free from As. The charge on the moving sintering grate is either ignited after both layers are spread on it, or the lower layer can be ignited and completely burned before the upper layer is charged. App. suitable for each method is described, with a horizontal blade for keeping the discharge from each layer sep., and sep. wind-boxes for collecting the flue gas from the *pre* that was heated sufficiently hot to drive off As. When double-layer sintering was carried out by the 1st method described, with a 3-in. thick bottom layer contg. only As-bearing ore, the feed used for it contained 0.034% As, and the sinter from it 0.009%. This sinter was used as 40% of the ore feed for the 6-in. thick upper layer, this feed thus contg. 0.012% As and having limestone mixed with it. The upper product was then self-fluxing and contained 0.008% As. In a test of the 2nd method described, the As content of the final self-fluxing product was 0.018%. George F. Comstock

Preventing arsine evolution from zinc smelting dross. National Smelting Co., Ltd. (by Philip M. J. Gray). Brit. 930,466, July 3, 1963, Appl. July 6, 1960; 2 pp. Arsenical dross contg. chloride flux such as is formed in Zn smelting is stirred 10–15 min. into molten Pb at 600–50°, and subsequently treated 45–50 min. with 6–10% H_2O, to prevent deliquescence and AsH_3 evolution on standing in moist air. The molten Pb bath probably removes metallic Zn from the dross, thus decreasing the acidity of the surface fluid formed on standing. Better results are obtained by mixing nonarsenical dross with the other dross in the Pb bath. When this was done before both the Pb and the H_2O treatments, in recovering from 500 lb. dross Zn 300, Pb 77, Cl 19, and As 2.2 lb., AsH_3 in the exhaust air was 92 p.p.m. total, and 6 p.p.m. final. George F. Comstock

Behavior of arsenic during oxidizing roasting of Kerch iron ores. N. A. Vasyutinskii and L. I. Vasyutinskaya. *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk, Met. i Gorn. Delo* 1963, No. 1, 26–32. Samples of hydrogoethite-ferrichlorite-siderite ore contg. 0.10–0.13% As were subjected to oxidizing roasting at various temps. The role of sorption-desorption processes in extn. of As during oxidizing roasting was studied. During roasting As begins to come off at >800°. At 900–1000° most of the As migrates from the oolites into the ore bond. This is attributed to sorption of As by aluminosilicates. Addn. of sorbents (clay, activated clay, dolomite, gypsum, alumina gel, silica gel) increased the extn. of As at all roasting temps. Gypsum was the most efficient. 58:13495f ——CA——

Metallurgical treatment of cobalt-bearing arsenopyrite. I. Mineral composition. Yasuaki Ueda (Kyushu Tech. Coll., Japan). *Kyushu Kozan Gakkai-shi* 31, 78–81(1963). An arsenical ore was used which consists mainly of arsenopyrite and pyrite with small amts. of chalcopyrite, sphalerite, and Bi mineral. Its table concentrate contains Co 1.26, As 40.80, Fe 33.60, and S 21.35%, and the flotation concentrate gives lower arsenic and Co contents. These concentrates were studied by means of chem. and differential thermal analyses, thermogravimetric methods in both vacuum and neutral atm., x-ray powder method, and microscopic observation. Co is not found in pyrite, but only in arsenopyrite. The most Co was substituted in arsenopyrite in place of Fe and the rest was present as cobaltite. II. Distillation of arsenic at low pressure. *Ibid.* 124–33. The As-removal mechanism of Co-bearing arsenopyrite by thermal decompn. was studied. The product condensed in the hottest portion of the retort was cryst. As. It was followed by dark-red fused As and then As_2S_3. The distribution of the condensate depends on amt. of pyrite in arsenopyrite. The As-removal efficiency was >38%, and the residue was FeS. The crude As contg. a small amt. of S was then refined to obtain pure As, and 99.9% As was obtained with 60% recovery by differential distn. and magnetic sepn. The As contg. more S was subjected to oxidizing roasting and As_2O_3 99.9% pure was obtained. 58 : 13493c Kinjuro Aso

Pyrite roasting process. Metallgesellschaft A.-G. (by Rudolph Hess). Ger. 1,139,521 (Cl. 18a), Nov. 15, 1962, Appl. Oct. 21, 1961; 4 pp. In a process for roasting pyrites contg. volatile components, e.g. As, Pb, Zn, or Cd, the volatile substances are evapd. in an initial roasting step in a shelved roasting furnace, the final roasting step being conducted as a fluidized-bed process. The fluidized-bed roasting step is divided into 2 substeps of different capacity, whereby in the 1st sub-step the after-roasting is conducted, the roasting gases of this step being collected sep.; the 2nd step is operated with an excess of air so that a roasting gas ≥600°, contg. 5–8% SO_2 and the resp. amt. of O, is obtained, which is passed into the shelved furnace after dust removal at elevated temps. and addn. of fresh air. Preferably, the roasting gases of the shelved furnace are passed into an electrostatic gas purification unit. 58 : 9231d Friedrich Epstein

Roasting of ores of the Khoru-Aksy deposit. M. A. Gavrilov. *Tsvetn. Metal.* 35, No. 8, 47–9(1962). Complex Ni–Co arsenides are roasted in a lab. tubular elec. furnace in a CO_2 atm. contg. 10% CO, and then leached in a soln. contg. NH_3 and CO_2. The best roasting conditions were 2–3 hrs. at 800°. After leaching the calcine with NH_3–CO_2 soln., the extn. was Ni 97, Co 94, and As 12%; ~19% of the As was eliminated in roasting, and the balance remained in the filter cake. This compares favorably with the 70–80% As recovery in soln. on autoclave treatment of the ore. 58 : 4208h E. M. Elkin

Sulfation of metallurgical dusts in oxygen-enriched air. L. S. Getskin and V. P. Savraev. *Tsvetnye Metally* 34, No. 11, 26–9(1961).—Metallurgical Pb dust contg. Se 0.24 and As 3.3% was granulated with H_2SO_4 and roasted in a lab. fluidized-bed furnace at 350–400°. Increasing the O content of the air to 30% markedly increased the degree of volatilization of Se, As, Zn, and Cd, and decreased the S content of the scrubber mud. The mud contained Se 10–15 and S 5%. Further enrichment of the air with O was of little effect. 56 : 11279c E. M. Elkin

Continuous sulfuric acid manufacture by roasting of sulfide ores, especially pyrites. Vladimir Sojka, Oldrich Liska, and Emil Ryttnauer. Czech. 93,425. Appl. Aug. 29, 1958. If roasting, followed by catalytic oxidn. of SO_2, is carried out at 6 atm., the degree of $SO_2 \rightarrow SO_3$ conversion is increased, the amt. of noxious exhaust gases is decreased because of better utilization of SO_2, and catalyst poisons (As, Se) are removed from the combustion gases owing to the operation at 80°. 56 : 8239-f D. S. Kasik

Removal of arsenic, antimony, and sulfur from iron compounds, iron ores, and iron in pellet or lump form. Karel Niemiec. Czech. 91,020, June 15, 1959. The pellets are spread out as a layer, their size being ≤2 mm. Through this layer, a reducing gas, e.g. blast furnace is passed. The As, Sb, and S are removed as volatile compds. This removal is promoted if heat is applied externally to the layer, and also if steam is blown through it. Werner Jacobson

Elimination of arsenic from Kerch ores. V. A. Sorokin and F. V. Bulgakov. *Domennoe Proizvodstvo, Sbornik Statei* 1958, 36–42(Pub. 1959).—The basis of the proposed method of As elimination is the principle of chloridizing roast in the sintering process with the formation of easily volatilizable As chlorides. Harmless K–Na chloride salts as powder or aq. soln. are used as the chloridizing agent. In lab. expts. the As content was decreased by 79.6%. At the same time, when 2.5–3.7% sylvite was added to the charge, the P content was decreased by 30–40%. Addn. of sylvite intensifies the burning process and increases the thermal effect. This is explained by the catalytic effect of the alk. salts of sylvite. From *Referat. Zhur., Met.* 1960, Abstr. No. 14097. 55 : 13225e E. M. Elkin

Removing arsenic from fine, roasted iron ore. Metallgesellschaft Akt.-Ges., Brit. 835,794, May 25, 1960. As_2O_3 is volatilized from Fe oxide ores, and sintered to enlarge the particle size, by heating to at least 800° in an atm. as nearly neutral as possible, with an exclusively solid reducing agent consisting of sulfide equiv. to 1–4% FeS_2, based on ore wt., and coal equiv. to 1.8–3.6% C, similarly based, but exclusive of fuel burned. The atm. should contain less than 2% O and no reducing gas, and the ore should not be reduced further than to Fe_3O_4. The reducing agent preferably is composed of 1/3 pyrites and balance anthracite, unless the ore contains sulfide. In carrying out the process on a moving, sintering grate, up to 6–9% C may be required to provide fuel for heating, but it is preferred to obtain 1/3 the heat from hot combustion gases. The air supplied, at least for the 1st half of the processing period, should not be over 10 cu. m./sq. m. grate area/hr., but toward the end of the grate travel it may be 50–80 for effective sintering of 5–7 tons/sq. m./day with 20–40-min. heating. The final As content should be <0.03, and final S should be <0.3%. A roasted flotation ore contg. 1.7% As and 1.48% S, 95% finer than 2 mm. and 43% finer than 0.06 mm., was pelletized with 4% pyrites and 6% coal corresponding to 1.8% C, to 10–20 mm. size, and the pellets were deposited 35 cm. deep on a 10-cm. layer of preroasted pellets on a 40 by 40-cm. grate. Hot combustion gases contg. no O were drawn through the bed at 1230°, and the final product contained 0.08% As and 0.2% S. George F. Comstock 54 : 22510

Lead and arsenic report. D. J. Blythe. *J. Air Pollution Control Assoc.* 10, 296–343(1960).—In view of the toxic properties of Pb and its alloying constituents, particularly As, most of the secondary Pb plants in the U.S. have adopted methods to eliminate these elements from stack emissions. Usually, the gases from the furnaces are cooled and fume then filtered through cloth bags with a collecting efficiency over 99%. The temp. in the baghouse is kept high enough to prevent tar volatiles from condensing and blinding the bags. Lime is added to the emissions as they enter the baghouse to help prevent this. The collected dust in the bags is often over 50% metal. In some plants, provision is made for removal of odorous C–O–S compds. In refining and alloying of secondary Pb, baghouse filtering is generally sufficient. 54 : 21562 Roger W. Ryan

Volatilization process of contaminants from raw- and semi-product of lead smelting plant. L. P. Nafmark. *Trudy Inst. Met. i Obogashcheniya, Akad. Nauk Kazakh. S.S.R.* 2, 47–57(1960).—The results of expts. on volatilization at 200–1100° of various elements from raw- and semi-product of Pb-smelting plant examd. by spectral analysis were described. Hg appeared the most volatile contaminant and evapd. entirely at temps. up to 600°. Tl started to vap. at 300–450°, and at 600–700° its concn. in volatilization product reached a max. Cd appeared in volatilization products simultaneously with Tl, and evapd. at a wide range of temps. In appeared in the volatilization product at 800°, and its evapn. characteristics were similar to that of Sn. Te began to evap. from concentrate and agglomerate at temps. above 900° and from the dust at 300–500°. The evapn. curves of As and Sb were alike and showed 2 max. at 350 and 900°. Ga and Mo were present in very small concns. and were revealed in fractions formed at 500–600°. 54 : 20737a W. Tomaszczyk

Speiss treatment by sublimation under vacuum. V. N. Esterov and R. A. Isakova. *Izvest. Akad. Nauk Kazakh. S.S.R., Ser. Met., Obogashcheniya i Ogneuporov* 1958, No. 3, 53–60.—Vacuum sublimation, which permits a sufficiently complete sepn. of all volatile constituents of speiss into a sublimate, and concn. of Cu and noble metals in the residue, was investigated. Expts. were made with speiss contg. Cu 31.04, Pb 10.81, As 17.2, Fe 22.95, Sb 1.5, Zn 3.56, S 2.3, Cd 0.06, and In 0.003%, and Ge trace. The effect of temp., sulfiding agent consumption, time, and residual pressure on the degree of As, Sb, and Pb sublimation was investigated. On heating speiss mixed with elementary S, almost complete volatilization of Sb, As, and Pb from the speiss is obtained at 800°, 1 hr., 0.1 mm. Hg residual pressure, and S consumption equal to the wt. of speiss. On heating speiss mixed with pyrite, practically complete volatilization of Sb, As, and Pb occurs at 900°, pyrite consumption equal to 200% by wt. of speiss, 0.1 mm. Hg residual pressure, and 1 hr., or at 950° and pyrite consumption 80% by wt. of speiss, in the same time. From *Referat. Zhur., Met.* 1959, Abstr. No. 17267.
54 : 18254a E. M. Elkin

Removal of volatile components, especially arsenic sulfide. Metallgesellschaft Akt.-Ges. (by Franz Schytil). Ger. 1,028,344, Apr. 17, 1958 (Cl. 40a). Small amts. of fresh material are fed intermittently into a hot fluidized bed contg. no volatile components. The next portion of fresh material is added only after the temp. and the expn. of the fluidized bed has attained approx. the original values. For driving off As, pyrite is preferably used. From *C.Z.* 1959, 6947. 54 : 19263a Otto Smetana

Harmful waste products from the copper-smelting industry in the Central Urals. L. V. Timofeeva. *Voprosy Gigieny Truda, Profpatol. i Prom. Toksikol.* 2, *Sbornik Sverdlovsk.* 5–16(1958).—The prepn. of Cu from the sulfide ores is accompanied with the discarding into the atm. of larger quantities of SO_2 and dust which contains Pb, Zn, Cu, As, etc. A study was made of the air in 2 regions around the smelting plants. In these regions a southwesterly wind, 3–5 m./sec., prevails. The methods of sedimentation and aspiration were used at 2–4 km. from the source of the waste products with the subsequent analysis for As, Zn, Cu, Pb, chlorides, nitrogen oxides, and S compds. All of the samples contained SO_2 and toxic dust in a concn. which far exceeds the acceptable limits. The concns. vary over a broad range, depending on the height of the source and the wind velocity. There was also an increase in the incidence of respiratory diseases in this region over that in a control region. From *Referat. Zhur., Geofiz.* 1959, Abstr. No. 3970.
54 : 12438d

Removal of arsenic from sulfidic ores. Metallgesellschaft Akt.-Ges. (by Hermann Meininger, Rudolf Michels, and Wilhelm Hess). Ger. 1,023,592, Jan. 30, 1958 (Cl. 40a). The ores, e.g. chalcopyrites, are heated to 600–800° in a rotating, direct-heated kiln before roasting. From *C.Z.* 1959, 4958. 54 : 10792a Kurt Mann

Introduction of the process of sulfatization of lead dusts. L. S. Getskin, A. G. Batyuk, P. P. Tsyb, R. I. Gorokhvodatskaya, V. P. Savraev, V. P. Zinov'ev, V. G. Fel'dman, A. V. Bratchik, and V. P. Polulyakh. *Tsvetnye Metally* 32, No. 10, 35–42(1959).—App. and process for the sulfatizing treatment of metallurgical Pb dust are described. H_2SO_4 (92%) is used for the granulation of the dust, contg. Pb 49.3, Zn 10.3, and Cd 2.5%, in a bowl-type granulator. The granules are roasted at 350° in a fluidized-bed furnace to volatilize most of the As, Se, Cl, and F. The roasted product is leached with water. The extn. into soln. is Zn 97 and Cd 95%, and 98% of Pb remains in the residue. 54 : 7476h E. M. Elkin

Removal of arsenic from ores, especially iron ores. Ludwig Stahl. Ger. 961,632, Apr. 11, 1957 (Cl. 18a, 1m). To remove As, the ores are well ground. The granulate is mixed with 7.5–10% petroleum coke of the same particle size and then roasted at 550–700°. The distd. As is pptd. in chambers. The processing is preferably carried out in Dwight-Lloyd app. 53 : 11684g H. Reiners

Recovery of sulfur from hot, sulfur-containing gases. Duisburger Kupferhütte. Brit. 755,182, Aug. 15, 1956. S is recovered by cooling the gas stream to within 10° of its dew point, removing particles of liquid and solid impurities by cooling just below the dew point, and then removing the pure S at another cooling stage. Thus, 2900 cu. m./hr. (at normal temp. and pressure) of exit gas contg. 90% SO_2 and 6% S leaves a roasting furnace at 620°. The gas is cooled to 300° and then led into a separator held at 285–92°. Here, FeS 8, As_2S_3 6, PbS 5, Sb_2S_3 1, Se 0.2, and elemental S 50 kg. are sepd. per hr. The gas leaves at 282–5° to a heat exchanger which brings the temp. to 125°. Thus 370 kg./hr. of elemental S contg. less than 0.2% As and 0.5% metal sulfides is produced. The exit gas, primarily SO_2, is recycled to the roasting furnace. Albert Howard Cohen

Mat from arsenical sulfide cobalt ores. Philip B. Dettmer and Lyall J. Lichty (to Quebec Metallurgical Industries Ltd.). U.S. 2,741,553, Apr. 10, 1956. Arsenical Co-S ores, which yield slag and speiss under normal furnace conditions, are made to yield a slag and mat by maintaining an As:S ratio of ≤1 in the furnace feed. Thus, a feed contg. Co 5.43, Ni 1.66, Cu 1.64, Pb 1.15, Fe 15.69, As 13.81, S 15.95, CaO 10.00, SiO_2 8.09%, and 276.14 troy oz. Ag/ton yielded a mat contg. Co 11.3, Ni 3.48, Cu 3.42, Fe 29.18, As 3.8, S 28.50% and 575.0 oz. Ag/ton. The metal recoveries in the mat were Ag 96.33, Co 96.27, Ni 96.98, and Cu 96.47%. The bulk of the As was recovered in the baghouse dust. More As was found in the slag than in the mat. The As content of the mat was a linear function of the As:S ratio in the furnace charge. At ratios of 0.5 and 2.4, the As in the mat was 1 and 13%, resp. With an elec. furnace, best results were obtained when electrodes were just out of contact with the surface of the molten bath.
50 : 16645a C. H. Fuchsman

The desarsenizing roasting of tungsten ore. Genichi Nakazawa, Tadayoshi Koizumi, and Kiyoshi Terunuma (Resources Research Inst., Kawaguchi). *J. Mining Inst. Japan* 72, 75–80(1956).—Roasting scheelite in an oxidizing atm. in order to volatilize As_2O_3 was not very successful because nonvolatile arsenate was formed; 50–70% was removed at 700–1000° in 1 hr. Roasting in N_2, CO_2, and SO_2 almost completely volatilized As_2O_3 at 900–1000° in 1 hr. The fluidized-bed technique was used. Flotation concentrate of −325 mesh was stably fluidized together with 60–100-mesh pyrrhotite. 50 : 16597h Hideaki Chihara

Washing and cooling of gases containing sulfur dioxide. Chemiebau Dr. A. Zieren G.m.b.H. Brit. 744,465, Feb. 8, 1956. Roaster and combustion gases contg. SO_3 are cooled and freed of dust, SO_3, and compds. of Fe, Zn, Pb, Se, and As by scrubbing with a suitable liquid, e.g. H_2SO_4, in 2 or more stages. The scrubbing liquid from the 1st stage is cooled by evapn. of water in a vacuum evaporator, in a tower in which the liquid is sprayed into a current of air, in a rotating tubular crystallizer through which air is passed, or by passage over a pile of acid-resistant shapes. The solid, e.g. As_2O_3, that crystallizes from the cooled liquid is removed by sedimentation, and the liquid is returned to the scrubbing tower. For example, 12,000 cu. m./hr. of gas contg. 10% SO_3 and considerable As_2O_3 was washed and cooled from 400 to 78° by spraying into the gas 23.3 cu. m./hr. of 45% H_2SO_4. The H_2SO_4 left the tower at 78°; 12.5 cu. m./hr. of the acid was passed through a vacuum evaporator in which 790 kg./hr. of water was removed and 135 kg./hr. of As_2O_3 was settled out. The cooled acid was mixed with the rest of the scrubbing acid, and the mixt. was returned to the scrubbing operation at 55°. J. C. Brosheer

50 : 13911 e

Treating arsenical sulfide cobalt ores. Lyall J. Lichty (to Cobalt Metallurgical Industries Ltd.). Brit. 746,521, Mar. 14, 1956. Concentrates, placed on banks of an arc furnace are heated to the b.p. of As sulfides and of As, but below the b.p. of the charge and allowed to run to the bottom to form a mat contg. <3% As. The latter is ground until 80% passes through a 200-mesh screen and is roasted in air at. 500–550°, for 1 hr. The roasted mat is mixed with about 10% H_2O and 33% H_2SO_4 by wt., allowed to react, dried, and roasted in air at about 620°. The temp. is increased to that desired in 2 hrs. and held there for 1.5–2 hrs. The time of the last roasting is adjusted to obtain a Co:Fe ratio of at least 4:1 in the soln. by leaching the roasted product with hot water. Addnl. roasting time is of little effect on either the Co:Fe ratio or the Co extn. The process volatilized about 90% of the As and concentrates >90% of the Co, Ni, and Cu in the mat. 50 :12795e J. D. Gat

Agglomeration of iron ores. Compañía Nacional de Piritas S.A. Span. 224,074, Dec. 2, 1955. Granulated Fe-contg. minerals and flotation concentrates, uniformly mixed with 10–25% of 0–4 mm. ground pyrites as a combustible instead of the usual C, are sintered. Their As impurities are then removed by volatilization while the S is oxidized to SO_2 at a low temp. in the sintering app. Preroasted pyrites contg. 20–5% S give the best results, although satisfactory results are also obtained with ordinary Fe pyrites. If alkali metal or alk. earth chlorides are added simultaneously, partial elimination of other metallic impurities is achieved, producing low-S agglomerates suitable for production of high-quality iron. 50 :11920c Alberto H. Adams

The distribution of arsenic among the products of the lead industry. L. M. Kabanova. *Vestnik Akad. Nauk Kazakh. S.S.R.* 11, No. 8, 68–73(1955).—Material balances for As in the lead industry were constructed from industrial data for agglomeration (I), smelting (II), and refining (III) operations. For I, 46.7% of the total As is introduced as Pb dust from Cu smelting (contg. 4.94% As); and 25.4% enters as PbS concentrate (0.17% As). The agglomerate contg. 0.40% As) accounts for 57.5% of the As feed to II, while dross (3.25% As) constitutes an addnl. 33.6%. The unrefined Pb leaving II (0.68% As) contains 35.7% of the As charged into the smelter. The mat (1.40% As) from II contains 18.2% of the total As. Mech. losses and wastes account for 19%. Refined Pb from III is As-free, while the dross contains 95.6% of the As fed to the refining stage. K. recommends that the dross not be recycled in the Pb operations. It should be separately processed to recover the products. Speiss (contg. 26.60% As) obtained from II should be worked to recover Pb, precious metals, and As as com. products. 50 : 7034f C. H. Fuchsman

Arsenic-free elemental sulfur and sulfur dioxide from pyritic ores containing arsenic. Instituto Nacional de Industria. Span. 208,450, Jan. 30, 1954. Pyrites (I) which contain As are heated first in a furnace in the presence of SO_2 at 500–50°. At this temp. the As volatilizes as S_2As_2, which is easily condensed. In the 2nd step, I are heated by the same gases to 700°, and the FeS_2 loses part of its S, which is easily condensed in a pure form. The FeS_2 is transformed into Fe_7S_8. In the third step, the Fe_7S_8 is roasted to give pure SO_2 in the presence of air, O, or their mixt. The SO_2 is recycled to the 1st step. Werner Jacobson

Removal of arsenic from pyrites. Instituto Nacional de Industria. Span. 208,449, Jan. 30, 1954. Pyrite (I) is treated with gaseous SO_2 at 500–550°. The As distils out as a compd. which has the approx. compn., S_2As_2. The S_2As_2 can be easily condensed, sepd., and purified. There is no risk of any loss of S, as I loses the S only at temps. of 700° and higher. The removal of As and the roasting of I can be done in one operation in a suitably constructed furnace, where the I is moved from one zone into the next as in a fluid bed. The SO_2 used can be part of the gas obtained in roasting the I. 49 : 7206c Werner Jacobson

Autogenous roasting of sulfide-ore concentrates. New Jersey Zinc Co. Brit. 701,555, Dec. 30, 1953. Cd, Pb, As, Ag, and Au components of a Zn-Fe-Cu sulfide concentrate are volatilized during roasting at 1050–1200° in a vessel which rotates about its horizontal major axis by the introduction of high-pressure air at selected points among the moving concentrate pellets in the vessel so as to establish and maintain several noncontiguous hot zones differing in temp. by 50–100°. Removal of volatilized components is facilitated by delivery of the roasting air downward into the moving pellets. Recovery of volatilized components is effected without the use of added agents like chlorides. A wide variety of Zn-Fe ores can be handled. W. A. M.

Simultaneous recovery of metals and sulfur from metal sulfides. G. A. Odéen, Rignor Svendsen, Lilly Hauger, Georg Odéen, Wera Kvebaek, and Margareta Berg-Nilssen. Norw. 83,374, Mar. 22, 1954. Sulfide ores are heated with C and CaO or Na_2CO_3 in an atm. of CO to a temp. at which the metal produced is in a molten condition. CaF_2 or $CaCl_2$ is used as a flux in an amt. sufficient to give a fluid CaS or Na_2S slag. The slag is treated with steam and CO_2 to recover the S and alkali, e.g. by boiling the slag in water while passing in CO_2. In an example, pyrites are heated to drive off S, and the residual FeS is heated with CaO, CaF_2, and C in an electric furnace to give Fe, CaS-CaF_2 slag, and CO. The slag is then treated with steam and CO_2 to give $CaCO_3$, CaF_2, and H_2S. The H_2S is passed with air over an Fe_2O_3 or bauxite catalyst to give S in 85% yield. A complex pyrite is heated to drive off S and As_2S_3 and smelted with CaO, CaF_2, and C. Zn distils off and Fe, Ni, and Co are tapped from the bottom of the furnace. A Pb or Pb-Ag layer seps. below the Fe layer, but Cu remains in the slag as Cu_2S. The slag is heated in a high-frequency elec. furnace with CaC_2 and CaO to give Cu and a CaS slag which are sepd. and the latter treated with steam and CO_2. Another example describes the smelting of PbS with Na_2CO_3 and C with regeneration of the slag as before.
48: 8150f R. D. Satchell

Refining of ores high in arsenic. Takeo Watarase, *et al.* (to Gakuta Industries Co.). Japan. 57('53), Jan. 9. Powd. Ni ore is mixed with 5–10% bleaching powder, heated in a reaction tube at 300–400° while passing through Cl gas to vaporize $AsCl_3$ and $SbCl_3$. The residue contg. $NiCl_2$, $FeCl_3$, $CoCl_2$, $CuCl_2$, $PbCl_2$, etc., is dissolved in warm water and the ingredients sepd. by a wet method. K. Kitsuta

Sulfuric anhydride from pyrites. Lavre Fassina and Louis Fassina. Brit. 655,327, July 18, 1951. SO_3 is produced by heating a mixt. of pyrites and an oxide of Mn, preferably Mn_2O_3 or MnO_2, in a furnace at not less than 700°. Addnl. products are $MnSO_4$ and Fe_2O_3. By heating the mixt. slowly to 400° and passing a current of air into contact with it, impurities, such as Sb and As, are evolved in the form of gaseous oxides. The temp. is then raised to 700°, and the SO_3 vapors are evolved. 46: 4135e P. J. Wilson, Jr.

Arsenic removal from lead concentrate by powder roasting with pyrites. Franz Brenthel (Zvecan/Srbiya, Yugoslavia). *Erzbergbau u. Metallhüttenw.* 3, 290-6(1950).—For effective As removal the presence of pyrites is essential. The pyrites content during the preroast prepn. must be at least 10% of the wt. of the galena, if the concentrate contains up to 2% As. "Isomorphous" As is more difficult to volatilize than As in free arsenopyrite. Arsenic volatilization by roasting in the presence of pyrites begins at 450° and attains its optimum at 650-700°. Above 700° the concentrate begins to burn, Pb volatilization rapidly increases, and As evolution diminishes rapidly as a result of arsenate formation. Arsenic removal is most complete by exclusion of air with inert gas. By roasting with pyrites, As content can be reduced from 2 to 0.16%, from 1 to 0.13%, and in the case of "isomorphous" As from 0.5 to 0.16%.
45: 89d H. Stoertz

Removal of sulfur, phosphorus, and arsenic from gases. Huay & Cie. Brit. 603,735, June 22, 1948. Gases unreactive to Cl are purified from S, P, and As compds. by adding Cl to the gas stream in amt. sufficient to produce enough hypochlorite to oxidize the impurities when the gas mixt. is passed through H_2O contg. alk. earth or Mg carbonates. 43: 2382a Howard W. Kruse

The manufacture of hydrogen sulfide. I. The reaction between hydrogen and pyrites. L. M. Clark and H. M. Spittle (Imp. Chem. Inds. Ltd., Winnington, Eng.). *J. Soc. Chem. Ind.* (London) 67, 5-8(1948).—Good yields of H_2S are obtained by reaction of pyrites (up to 1.5-in. mesh) with H_2 at a temp. of 625-50° and a space velocity of 40-50. Equipment corrosion is minimized by use of mild steel servarized with Al. H_2S concns. to 93.5% can be obtained but a max. of about 80% is advisable to prevent S distn. Removal in the exit gases of 90-98.5% of the As present in the pyrites is effected.

Removal of fluorine, chlorine, and other contact poisons by washing of gases to be electrically dearsenisted. Metallgesellschaft A.-G. Belg. 449,725, April, 1943. The gas is passed successively through a 1st washing tower, a liquid separator, a 2nd washing tower, a 2nd liquid separator, and finally to the dearseniating chamber. The acid removed in the separators is returned to the corresponding washing tower. A. Papineau-Couture

Removal of arsenic from roaster gases. Metallgesellschaft A.-G. Belg. 450,124, May, 1943. The roaster gases leaving the filter enter a tower at 400° and leave it at 200° to enter a second tower where they are sprayed with 60° Bé. H_2SO_4 and then a third tower where they are sprayed with 10° Bé. H_2SO_4. The acid from the second tower flows into sedimentation tanks and is then pumped to the top of the first tower where it is concd. to 56-58° Bé. and sent to a storage tank. A. Papineau-Couture

Purification of burner gas and sulfur losses in the acid division of the Archangel combine. G. M. Ginodman. *Bumazhnaya Prom.* 21, No. 5/6, 20-4(1946).—Lumps of S are burned in a rotary burner of 5 cu. m. capacity. Burner gases mixed with air are passed through a chamber for completion of the burning. The gases are then directed through a refractory-lined water-sprayed scrubber, where they are cooled to 300-50°. Thence the gases pass through an acid proof, brick-lined tower, packed to ⅓ of its height with 100-mm. Raschig rings. In this tower, irrigated with circulating weak H_2SO_4, the gases are cooled to 30-5° or lower. Also in this tower the gas is freed of dust, 56.4% of its SO_3 vapors, 50.4% of its As_2O_3, 57.6% of its Se and some sublimed S. The cooled and partly purified gas is passed through an elec. filter, which completes removal of original SO_3 to the extent of 99.95%, As_2O_3 to 99.93%, Se to 100%; sublimed S is not removed as nearly completely as the other impurities. Complete burning of S could be insured by properly regulating the quantities of S and air in the burner. Of the S charged into the burner, 8.2-10.6% is lost; 6.2-8.4% of this could be saved if proper control instruments were installed. Per 100 tons of S there are As_2O_3 400 and Se 40 kg. As_2O_3 must be disposed of to prevent water pollution. The Se is recovered for use in the electrotech. industry. 41: 2213c M. Hosch

Rotary kiln for gold ores and concentrates. A. C. McDonald. *Chem. Eng. Mining Rev.* 35, 24-5(1942).—The results of a series of tests on the roasting of pyritic Au ore contg. As and Sb in a 30 × 2-ft. rotary kiln are detailed. With an oil-fuel consumption of about 7% of the wt. of feed, the roasted charge left the furnace at about 950° with the elimination of 95-7% of the As, 92-6% of the S, and 25-30% of the Sb. Smelting of the clinker with $CaCO_3$ and PbO gave a Pb bullion contg. Sb 7, As 0.55, Cu 0.57%, and Au 6.9 oz./ton from original material contg. As 15, Sb 1.5%, and Au 1.4 oz./ton. B. A.

Removal of arsenic from gases containing sulfur dioxide. Fritz Lechler (to Metallgesellschaft A.-G.). Ger. 712,587, Sept. 25, 1941 (Cl. 12*i*. 24). The As is collected on the particles of a H_2SO_4 fog and the whole sepd., e. g., with an electrofilter. The SO_3 required for forming the H_2SO_4 fog is taken from the SO_3 gas and produced by oxidizing the SO_2 with O_2. 37: 4538c

Electric dearsenification of gases. Fritz Lechler (to Metallgesellschaft Akt.-Ges.). Ger. 709,894, July 17, 1941 (Cl. 12*i*. 24). To dearsenify the relatively cold and dry SO_3-contg. gases from converters or sinter installations used for the H_2SO_4 contact process, are simultaneously moistened and warmed to form a fog from which the As is removed electrically. The liquid used for moistening and warming the gases is kept warm by heat exchanging with the cooling water used for cooling the gases.

Dearsenizing smelter by-products. Gerhard Roesner and Helmut Ley (to Metallgesellschaft Akt.-Ges.). Ger. 650,520, Aug. 10, 1939 (Cl. 40a. 45.20). To remove As from smelter by-products (in order to utilize the by-product), the by-product is mixed with a reducing agent, moistened with H_2SO_4 and heated in a furnace. At 280° As_2O_3 starts to sublime and is completely removed at 420°. The reducing agents may be gaseous H, SO_2, CO, etc., liquids such as oil, or solid coal, coke, peat, etc. Generally 5-50% by wt. of H_2SO_4 is required, the exact quantity being detd. in each case. Instead of H_2SO_4, SO_2 may be used. The latter is passed through a heated mass of the smelter by-product, mixed with a reducing agent. As_2O_3 is obtained pure, even though Sb and Cd are present. 36: 2078^4

Removal of arsenic from oxidic ores. Josef Klärding. *Arch. Eisenhüttenw.* 14, 473–6(1941).—Arsenic occurs in oxidic Fe ores probably as iron arsenate. Magnetizing roasting of the oxidic ore removes 30–60% of the As; sintering twice removes 70–80%. As_2O_5 is formed by dehydration of arsenic acid at low red heat; it disintegrates then according to $As_2O_5 \rightarrow As_2O_3 + O_2$; the trioxide and metallic As are volatile, the vapor pressures increasing rapidly with temp. Metallic Fe reacts according to $As_2O_5 + 3Fe \rightarrow 3FeO + 2As$; the As formed is dissolved in metallic Fe. Therefore, to produce As-free Fe, As must be removed from the ore *before* reduction to Fe. This can be effected by temp. control and control of the grain size. Twelve references. 35: 5427[4] M. Hartenheim

Roasting and cyanidation of arsenopyrite concentrates. J. A. Walker. *Chem. Eng. Mining Rev.* 32, 122–4(1940).—Notes are given on the exptl. treatment of exceptionally high-grade arsenopyrite concentrates. Four lines of treatment were followed: (*a*) roasting of concentrate in air, (*b*) removal of As under N and subsequent roasting in air, (*c*) removal of As under SO_2 and subsequent roasting in air and (*d*) destruction of the Fe_2O_3 by soln. of calcine in acid. The calcine obtained was then cyanided. Each treatment is outlined. Conclusions include: (1) Roasting arsenopyrite concentrates in air, followed by cyanidation results in high-grade residues. (2) A high temp. "finish" improves the extn. of Au from the calcine. The removal of the bulk of the As under N, followed by roasting the resulting pyrrhotite in air gives calcine from which high Au extn. is possible, but in the plant such a method would be difficult to apply. The treatment that shows the greatest promise is oxidation of the concentrate under SO_2 to produce Fe_3O_4. This product is sol. in H_2SO_4 and the soln. of the Fe oxide leaves the Au free in the siliceous residue. This residue can be recovered by filtration and subsequently cyanided. 34: 1594[6] W. H. Boynton

Removing arsenic from iron ores. Mannesmannröhren-Werke. Ger. 643,202, July 26, 1937 (Cl. 18a. 1.03). Fe ores contg. As are completely or partly reduced with C at a relatively low temp., and the product, which contains As as Fe-As, is heated under oxidizing conditions, whereby As_2O_3 is volatilized. The process may be effected in a rotary furnace in which a reducing atm. is maintained in one part and an oxidizing atm. in another part.

Removing arsenic from ores and foundry products. Walter Savelsberg. Ger. 610,632, Oct. 26, 1935 (Cl. 40a. 2.20). Arsenic, present as arsenide such as Ni_2As_3, is removed as As_2O_3 by passing SO_2 over the ore, etc., at 1000°. The Ni becomes sulfide. $CaSO_4$ is added to assist in breaking down the arsenide. 30: 3393[2]

Removal of arsenic from lead blast-furnace charge by roasting will save retreatment of subsequent products. C. L. Oldright, Thomas B. Brighton and Donald P. Wilkes. *Eng. Mining J.* 135, 366–9(1934).—For removal by roasting As should be converted to As_2O_3 or As_2S_3; these are easily volatilized at low temps. Arsenic can be removed rapidly and completely from some arsenates by roasting with pyrite at low temps. Charcoal and coke have similar effects. The Wedge roaster with oxidizing atm. at the surface and reducing under the surface appears more effective in removing As than the Dwight-Lloyd furnace when a min. of extraneous carbonaceous fuel is desirable. Ca arsenate was the only common arsenate studied that remained stable under any of the treatments given. 28: 5791[8] W. H. Boynton

Smelting pyritic ores contaiing arsenic. Nils E. Lenander (to Patentaktiebolaget Grondal-Ramen). U. S. 1,962,802, June 12. Pyritic ore contg. As is smelted in a closed blast furnace, and the SO_2 produced is passed upward through highly heated carbonaceous material admixed with the ore so that it is partly reduced to elemental S. The amt. of carbonaceous material mixed with the ore is proportioned so that only such part of the SO_2 is reduced to S as is required to form As-S compds. with the As present in the ore, and the As-S compds. formed are condensed from the gaseous products which are withdrawn. 28: 4692[4]

Estimation of sulfur and arsenic removal from copper in the reverberatory furnace according to the laws of physical chemistry. Em. Lubojatzky. *Metall u. Erz* 30, 311–13(1933).—The fact that the concns. of sulfides and arsenides in the bath are inversely proportional to the sq. roots of their vapor pressures furnishes a basis for their detn. The application of the mass action law to the decompn. of sulfides and arsenides in the bath permits the development of laws according to which desulfurization and removal of As are dependent upon furnace temp. 27: 5283[3] H. Stoertz

Elimination of arsenic from iron ores. B. P. Selivanov, S. A. Pogodin, A. A. Zvyagin, E. Ya. Lipshitz and M. Ya. Jems-Levi. *Soobshcheniya Vsesoyuznogo Inst. Metal.* 1931, Nos. 3–4, 54–67.—A study of the possibility of eliminating As from Kerchensk iron ores, contg. about 0.13% As on dry basis, by means of gases, was made from 3 angles: (1) temp., (2) nature of the gas and (3) nature of the As compds. in the ore. Parallel with this were also conducted expts. to remove As from artificially prepd compds. $As_2O_3Fe_2O_3$ and $As_2O_5Fe_2O_3$. In one series of expts. $As_2O_3Fe_2O_3$ was treated with a gas mixt.: Cl_2 10%, CO 20% and CO_2 70%, at 600°, 700°, 800°, 900° and 1000°. In another series, Kerchensk ore was treated with the same gas mixt. as above at 800°, 900°, 1000° and 1100°. In a third series, Kerchensk ore was treated with the gas mixt.: Cl_2 1%, CO 22% and CO_2 77%, at 800°, 900°, 1000° and 1100°. Cl_2 does not assist the removal of As and may even be detrimental. Therefore, in a fourth series of expts. Cl_2 was eliminated. Arsenic begins to diminish at 800° and reaches a min. at 1100°. The greatest removal of As from ore at temps. above 900° occurred in a gas mixt. $CO:CO_2$ = (25–30%):(75–60%), or in H_2O vapor when 5–10% coke was added to the ore. In this last case the CO and H_2 resulting from the H_2O and C reduce As_2O_5 to As_2O_3 or to As. Formation of AsH_3 is also likely. On treatment of the ore with a mixt. of $CO:H_2$ = 1:1 the removal of As is retarded. This can be explained on the ground that a partial reduction of Fe_2O_3 takes place, and the Fe absorbs As and retains it in the solid state. The above results will be used as a basis for a semi-commercial plant for the removal of As from iron ores. Tables and graphs (18) are given. S. L. Madorsky

Dust removal and electric purification of industrial gas. PIERRE POUTHIER. *Génie civil* 99, 263–5(1931).—The Cottrell-Lurgi process is very effective in removing As from the gas in the *manuf. of* H_2SO_4. 26: 2126² ANN NICHOLSON HIRD

Expelling arsenic from ores containing sulfur. A. G. P. PALÉN. Swed. 68,610, Dec. 17, 1929. Oxidation is repressed by heating the ore in vertical muffles in absence of air; the charge passes continuously down through the muffles, and As sulfides escape through side outlets. 26: 1890⁹

Smelting pyritic ores. PATENTAKTIEBOLAGET GRONDAL-RAMEN. Brit. 350,625, March 31, 1930. S and Cu and As are recovered from pyritic ores by smelting in a blast furnace with fluxes and solid reducing material in such proportion that a pyritic or a partial pyritic smelting takes place in the lower part of the furnace, while higher up the reducing material is at least substantially all consumed by SO_3, As_2O_3 and O to give elemental S and As, which are condensed on leaving the furnace. Various details of operation are described. 26: 952⁹

Reactions in the removal of arsenic from speiss by heating in the presence of pyrites. V. TAFEL AND H. W. LOOSE. *Metall u. Erz* 28, 422–5(1931).—By heating a mixt. of arsenides and pyrites in the presence of air, As can be completely removed. With a 1:1 mixt., the temps. required were 700–800° for Cu_3As, 900° for FeAs and 1000° for Ni_5As_2. FeS can be used in place of pyrites. The removal of As is attributed partly to the reducing action of SO_2 and partly to the decompn. of arsenates and arsenites by SO_2. In inert atms. such as CO, CO_2 and N_2, the As can also be removed by heating with pyrites, such volatile compds. being formed as As_2S_3 and As_4S_4. 25: 5182⁹ H. STOBBE

Removing arsenic from tungsten ore. JOSEPH H. BRENNAN (to Electro Metallurgical Co.). U. S. 1,790,088, Jan. 27. Free S is added to the ore and the latter is heated to above the b. p. of S and sufficiently high to volatilize the major portion of the As present. 25: 1210⁶

24: 1303⁹

Treating ores containing arsenic sulfide, pyrite and chalcopyrite. A. R. LINDBLAD. Swed. 66,711, Feb. 5, 1929. The ore is melted in an elec. furnace, the charge contg. S in such proportions that practically all the As is driven off in the form of S compds. The remaining product is worked further for the gaining of metals and eventually also S.

Treatment of complex speisses. PAUL PAPENCORDT. *Metall und Erz* 16, 6–13 (1919).—Results are reported of an investigation at the Institut für Metallhüttenwesen und Elektrometallurgie der Kgl. Techn. Hochschule Aachen on the treatment of speiss from the copper smelter at Oker, having the compn.: Cu 23.5, Pb 16.3, Sb 13.2, As 12.2, Fe 26.2, Ni and Co 2.9, Zn 3.1, S 2.1, and Au and Ag 0.12%. Previous methods are discussed and a new one is given. This is an adaptation of the process of Schilowski (*C. A.* 6, 977), in which copper ores containing As are smelted in an elec. furnace to volatilize As_2S_3. Samples of the above speiss were melted in 1-kg. batches in a graphite crucible arc-type elec. furnace, using varying quantities of pyrite to supply the S. Practically all of the As volatilized as the sulfide and condensed in a closed chamber but most of the Sb remained in the crucible, forming an antimony speiss with 25% Sb and 4% Cu, while 85% of the Cu went into a clean mat containing 25% Cu. A low-copper slag also formed. The As fume contained small amts. of sulfides of Cu, Pb, Fe and Zn and could be purified by resublimation in clay retorts at a red heat, forming an article of commerce. The Sb-speiss was smelted with Na_2SO_4 and C, giving a mass from which practically all the Sb could be leached as Na_3SbS_3 by water and the soln. electrolyzed to give metallic Sb by well known methods. The Cu mat contained most of the Pb, Ag, Au, Ni and Co; it can be treated by standard methods. Tests were made of pulverizing part of this mat and roasting in presence of silica, followed by smelting with the remaining mat to form black copper pig and lead silicate slag. 13: 1296⁹ O. C. RALSTON.

Apparatus for treating metallic ores. W. R. SMITH. Can., 182,070, Feb. 5, 1918. App. attached to a blast furnace is specified for condensing and collecting the As escaping from the furnace in gaseous form. 12: 672²

Apparatus for smelting cobaltite or other ores and collecting volatilized arsenic in water. W. R. SMITH. U. S., 1,349,226, Dec. 4. 12: 360²